リグニン討論会

第１回―第 63 回

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はじめに

リグニン討論会は 1956 年に発足しました。事務局も会長もなく、毎年世話人が交替しながら、この討論会が半世紀以上も続いて開催されてきたのは実に希有なことです。これはリグニンが、人々の科学的探究心を常に奮い立たせる魅力的な未踏峰の如き物質であるからでしょう。曾て世界のリグニン研究をリードしてきた欧米諸国の拠点の多くでは、近年の「すぐ目に見える研究成果」を求める風潮のなか、次第にその活動は寂れてきています。一方、日本では、毎年若い優秀な研究者がこの分野に参入し、厚い研究者層を形成して、樹木・木材科学分野で世界の研究をリードしつつあります。半世紀以上にわたるリグニン討論会の活動が、このことに大きく貢献していることは疑いのないことです。

高等植物は、リグニンの形成によってその大型化が可能となり、多様な進化を遂げました。そのため、リグニンおよびリグニン由来の腐植物質等は地球上最多の有機物となり、炭素循環の大きなプールとして、生態系の変遷に深く関わっています。したがって、リグニンに関する知見は、樹木や作物の生産・利用のみならず、人類生存圏の理解にとっても重要であります。しかしその化学構造さえも、天然有機化合物中最も複雑・多様であるため、未だ完全には解明されていません。いろいろな意味で未踏峰の連なる山脈のような未解明物質リグニンは、種々の異なる視点から異なる手法で見た断面の知見を総合することで、始めてその全貌を捉え得るものでしょう。そのため、リグニン討論会は、紙パルプ技術協会、日本木材学会、日本化学会、日本農芸化学会および繊維学会の共催、高分子学会およびバイオインダストリー協会の協賛学会となっており、異なる分野の研究者たちが、自由な討論を通してリグニンの全貌への理解を深めることを目指しています。このため、たとえ未完成の研究であっても、新しい着想や手法・技術、実験結果についての自由な討論が歓迎され、特定の学会の年次大会とは異なる性格を持っています。

リグニン討論会の講演要旨集には、その研究の最初の着想やデータが載ります。その後論文として発表されないものもあるので、貴重な文献です。審査済みの論文でなくとも、あるいは古い着想やデータでも、それがヒントになって優れた研究が触発されることは多々あります。この分野に新しく参入される研究者には、過去の講演要旨集を通覧することによって、リグニン研究の内容や手法の進歩・変遷を知り、巨大なリグニン山脈に立ち向かうための新しい戦略的発想の手掛りを得る「温故知新」の効果が期待できるかも知れません。　しかしリグニン討論会には公式の記録を残す事務局もなく、半世紀余の間には研究者の世代交代も進んで、古い講演要旨集は散逸しようとしています。そこで第 1 回討論会以来の全講演要旨集の原本を整備し、下記の研究拠点で保存公開することになりました。

★紙パルプ技術協会
★東京大学大学院農学生命科学研究科木材化学研究室（問合せ先、松本雄二）
★名古屋大学大学院生命農学研究科森林化学研究室（問合せ先、福島和彦）
★京都大学生存圏研究所（問合せ先、梅沢俊明）

そして約2000件を超える研究発表内容の検索を容易にするため、和文と英文とで発表題目、研究者名と所属を記録し、キーワードを本文内容から選定し、デジタル記録として整理しました。第35回討論会以降の要旨についてはキーワードの替わりに Abstract を記載しました。ただし重要なキーワードでも表題中に含まれる場合は、二重記録を避けるため省略してあります。各発表番号の最初の4桁は発表年次を、次の3桁は要旨集記載の発表番号を示しています。またリグニン討論会発足の経緯と変遷を知るための参考資料として、討論会発足の頃から深く関与して来られた3名の方々の特別寄稿を載せました。今後のリグニン研究のための参考資料として利用されることを期待しています。

この記録を整理するに当たっては、なるべく原著者を含む多くの方々にお願いし、点検・修正をして頂きました。貴重な時間を割いてご協力下さいました皆様に厚くお礼を申し上げます。なお、英文の表題、氏名，所属の誤訳・誤読、キーワードの選定などの責任はすべて編集世話人にあります。これらの記録は、原講演要旨集の検索の目的以外には、転用なさらぬ様にお願いします。~~さらに、誤字、脱字、その他修正を要する点などお気付きのときは、世話人宛お知らせ下さい。適時に修正版を下記の URL よりお配りして、正しい記録を皆様と共有したいと思います。~~

~~http://www.agr.nagoya-u.ac.jp/~lignin/Lignin_Symposium.pdf~~
（2018 年のリグニン学会設立により管理移管しました）

編集世話人、名古屋大学名誉教授　寺島　典二

リグニン(化学)討論会 開催記録

回	日時	開催地	講演	ポスター	特別講演	備考
1	1956.11.12	大阪、府立教育会館	16		0	
2	1957.11.15	東京、紙パルプ会館	20		0	
3	1958.11.04	福岡、九州大学農学部	15		0	
4	1959.11.13-14	京都、楽友会館	29		0	会期が 2 日間となる。
5	1960.11.19-20	名古屋、商工会議所	21		0	
6	1961.11.18-19	大阪、府立農林会館	19		1	
7	1962.10.04-05	札幌、北海道大学クラーク会館	24		1	
8	1963.11.05-06	松江、自治会館	18		3	
9	1964.11.11-12	東京、紙パルプ会館	22		2	
10	1965.11.08-09	大阪、科学技術センター	31		4	
11	1966.10.31-11.01	広島、広島大学会館	38		2	
12	1967.11.01-02	福岡、九州大学農学部	26		0	
13	1968.10.26-27	名古屋、名古屋大学農学部	28		0	
14	1969.10.28-29	東京、日本化学会講堂	20		0	
15	1970.10.08-09	札幌、市民会館	25		0	
16	1971.11.04-05	高松、電気ビル	34		0	
17	1972.11.04-05	京都、京都大学農学部	18		2	
18	1973.11.03-04	福岡、九州大学農学部	35		0	
19	1974.10.19-20	秋田、秋他大学教育学部	30		1	
20	1975.10.20-21	名古屋、名古屋大学農学部	34		2	
21	1976.10.18-19	東京、東京大学農学部	28	1+総合討論 1		
22	1977.10.08-09	札幌、北海道大学農学部	28	1+総合討論 2		
23	1978.11.01-02	松山、愛媛大学農学部	34		1	
24	1979.11.01-02	京都、生産開発科学研究所	30		2	
25	1980.10.17-18	福岡、九州大学農学部	32	1+総合討論 1		
26	1981.10.29-30	つくば、工業技術院筑波研究センター	32		2	
27	1982,10.21-22	名古屋、名古屋大学農学部	33		2	
28	1983.10.07-08	札幌、北海道大学農学部	30		1	
29	1984.10.15-16	東京、東京大学農学部	30		2	リグニン討論会に改称。
30	1985.11.06-07	高知、高知会館	34		2	
31	1986.10.21-22	京都、京大会館	35		2	
32	1987.10.20-21	福岡、福岡リーセントホテル	36		2	
33	1988.11.08-09	つくば、ホテルサンルート筑波	36		2	
34	1989.10.16-17	名古屋、名古屋大学農学部	37		2	
35	1990.10.15-16	東京、東京大学山上会館	36		1	英文 **Abstract** を記載。
36	1991.10.14-15	札幌、北海道大学学術交流会館	42		2	
37	1992.10.19-20	京都、京大会館	41		2	
38	1993.11.15-16	高松、四国電力 KK 総合研究所	39		2	
39	1994.10.12-13	福岡、福岡リーセントホテル	25	23	1	ポスター発表を開始。
40	1995.10.12-13	つくば、研究交流センター	26	18	1	
41	1996.10.03-04	名古屋、名古屋大学農学部	32	17	1	
42	1997.10.27-28	札幌、北海道大学学術交流会館	33	23	1	
43	1998.10.26-27	府中、府中グリーンプラザ	25	17	2	
44	1999.10.07-08	岐阜、岐阜大学農学部	29	19	2	
45	2000.10.26-27	松山、愛媛大学農学部	34	20	2	
46	2001.11.01-02	宇治、京都大学木質科学研究所	41	24	3	
47	2002.10.31-11.01	福岡、アクロス福岡国際会議場	34	17	2	
48	2003.10.30-31	福井、福井工業大学芦原学舎	35	27	2	
49	2004.11.18-19	つくば、筑波大学	27	17	1	
50	2005.10.19-20	名古屋、名古屋大学野依学術交流館	29	13	1 + パネル討論 1	
小計			1486	235	72	計 1793

回	日時	開催地	講演	ポスター	特別講演	備考
51	2006.10.26-27	北海道大学、学術交流館	28	30	2	
52	2007.11.14-15	宇都宮大学、大学会館	33	22	2	
53	2008.10.30-31	東京大学、弥生講堂	28	19	1	
54	2009.10.29-30	静岡県男女共同参画センター「あざれあ」	28	24	1	
55	2010.10.20-21	京都大学、百周年時計台記念館　国際交流ホール	30	20	1	
56	2011.09.15-16	山形大学農学部	28	19	1	
57	2012.10.17-18	福岡、アクロス福岡国際会議場	24	12	1	
58	2013.11.12-13	高松、サンポートホール高松	23	17	1	
59	2014.09.11-12	福井、福井工業大学	22	21	1	
60	2015.11.05-06	つくば、筑波大学	20	27	2	
61	2016.10.27-28	宇治、京都大学宇治おうばくプラザ	26	41	1 + 9*	*ワークショップ
62	2017.10.27-28	名古屋、名古屋大学野依学術交流館	18	29	3	
63	2018.11.1-2	小金井、東京農工大学	25	44	2	
総計			1819	560	100	総計 2479

1994年、第39回討論会、特別寄稿

「リグニン討論会の発足の頃」

九州大学名誉教授　千手諒一

リグニン討論会も今年で39回を迎えると言う。「10年ひと昔」と言います。40年も前のことを思い出すのは、82歳の翁には難儀なことです。かすかな記憶を頼りにベンをとってはみましたが、思い違いはお許し願います。

リグニン討論会の第一回目（昭和31年）は阪大工学部の八浜義和先生（故人）のお声がかりで聞かれました。当時は日本も、経済発展の真只中でありました。大東亜戦争で、エネルギーの総てを使い果した日本も、ようやく復興の波に乗り、朝鮮事変も重なって、復興景気に湧き立っておりました。3P 景気、3 白景気（紙、砂糖、硫安）と騒がれた時代です。製紙工場も増設また増設、勿論 SP 法ですから、蒸解廃液は垂れ流しです。公害問題は、早速田子の浦の汚染で始まりました。紙パルプ産業は四面楚歌で、私どもは肩身の狭い思いをしたものです。当時私は、九大の木材研究所で、キチン、キトサンの研究から SP 廃液中のリグニンスルホン酸のコロイド滴定を始めておりました。それがご縁で、八浜先生に親しくして頂きましたが、先生は木材化学工業に深い関心を持っておられました。ある時私に、「紙パルプ工業も木材の大半を流失するようでは、真の化学工業とは言えませんね」と言われました。農学部の学生時代から、工学部の応化にコンプレックスを感じていた私には、胸に突き刺さるひと言でした。私は廃液リグニンの利用を中心とした研究を進めて、木材の完全利用と共に、SP 廃液による公害を防止せねばと思いました。早速、八浜先生を初め東大の右田信彦先生（故人）、国策パルプの三川礼氏（後に阪大工学部教授）や佐藤孝一郎氏、九大木研の北浦貞夫先生（故人）、にお願いして、初回は阪大工学部で開くことになりました。初めの頃は、発表件数も少ないので、リグニンに関することなら何んでもよいと言うことで、パルプ蒸解のことまで発表されましたが、それでも数件で寂しいものでした。しかし回を重ねるにつれて参加者も段々増えて来ました。大学関係のみならず、工試（東京、大阪）の方々まで参加され、討論会も一段と活発になってきました。私なんか、わざわざあるマイクも使わずに口角泡を飛ばしたものです。中野さん（東大）、越島さん（大阪工試から京大木研）、林さん（立命館大）、猪狩さん（東京工試）などなど、懐かしいご仁が大勢でした。この討論会の魅力はなんと言ってもその会の雰囲気でした。参加者全員が、恰も一家族のように、心おきなく語りあえる。その喜びは他の学会では到底味あうことのできない大きな魅力でした。メンバーの各人は、年一回のこの討論会を楽しみに、日々研究に励んでいたように思います。リグニン討論会が、39 回を数える今日もなお、旧に倍して盛大であるのも、一因がその辺にあるのかもしれませんね。しかし時は流れて、パルプの製造法も KP 法に変わりました。廃液リグニンは、公害の元になる廃物ではありません。燃料として立派に利用されておりますから、パルプ工業も真の化学工業と言える時代になりました。リグニンの利用研究も、そろそろ看板を下してもよい頃かと思っておりましたが、今回のプログラムを拝見して安堵致しました。これからはリグニンの生化学を中心に、リグニンの本質を明らかにしたいものです。リグニンのない木材などは無理だとしても、丸太の木材をそのままシートに変えることができれば最高ですね。ナインテイ（90）、ナインテイ（90）、ナイン（9）の収量、白色度、強度を目標とするリグニンのメカノケミカルの研究も進められている由、私は大きな期待を寄せております。リグニン討論会の進路も、時の流れと共に、大きく変わりつつあることをこの上なく嬉しく思います。皆さんの御研鑽を祈ります。

2005年、第50回討論会　特別寄稿

「リグニン討論会の黎明」

京都大学名誉教授　越島哲夫

寺島先生の、本当に先生らしい純粋なご提案に賛同しながら、この討論会はそもそも誰が、どんな経緯で始めたのかを、先ず知りたいと思って、私なりに努力してみました。当時私は、京大木材研究所の助手をしており、大凡のことは解っているつもりでしたが、調べてみると、かなり誤っていたようです。

第1回の討論会は、皆さんもご承知の様に，阪大、八浜義和先生のところでした。八浜先生が日本化学会に要望書を出して“リグニン化学討論会”が発足したのには千手諒一先生〈当時九大生産科学研究所助教授〉と八浜先生の出会いが一つのきっかけになった（坂田功氏）ようです。もう一人、設立に当って外せない人は、当時、国策パルプ〈株〉農林科学研究所の三川礼先生（のちに阪大教授）です。三川先生もその頃、八浜先生に討論会をつくることを強く要望されていたのではないかというのが私や林アキラさん（のちに立命館大教授）の推測です。その結果、八浜（阪大）、西田（九大）、右田（東大）、舘〈京大〉先生が発起人となり、リグニン化学討論会がスタートしたようです。第 1 回討論会の開催には当時阪大助教授だった京極先生が奔走され、16 件の発表がありました。この時、企業からは国策パルプのみで、3件の発表があったのも，三川先生のリグニン化学への情熱が現れていたようにおもえます。第1回では、当時、大御所といわれた，八浜、右田，舘、北浦、大野（一月）各先生のほか、近藤（民），千手、三川、軒原，佐藤（孝）、石川、中野、榊原、本田（真）、京極など錚々たる名前がならんでいます。第 2 回は東大において右田-中野先生で、第 3 回は九大、第 4 回は京大で行われました。九大では、北浦-千手先生で実施され、千手先生が世話人として大変努力された（坂田功氏）と聞いています。京大では、林アキラさんが世話人を任され、この時始めて企業からの参加を呼びかけ、寄付も募った結果、発表数が増えたので会期を二日間とした（林アキラ氏）ようです。同時に懇親会も加え学生は無料としたのも第 4 回からでした。第 2 回の、東大での討論会には私、欠席したので詳しい情報は私の所になく、寺島先生から補足して頂ければ幸いです。何れにしろ創世期のころは大学を代表する大先生のほかに、実際の運営に当った世話人各位の情熱と努力がこの討論会の維持と発展の大いなる原動力となったことは記録されるべきでありましょう。

ここで私は、あまり知られていないと思われるので、もう一度三川先生について触れておきたい。先生は国策パルプ時代、昭和 26-31 年にかけ、当時有名であった三川理論を展開された。それは，X 基、Z 基、B 基となずけられた、リグニンの反応性の異なる官能基がサルファイト蒸解やクラフト蒸解でどのように挙動するか、そして脱リグニンが進行するかを示したもので、当時としては理路整然として真に興味深いものでした。私は後になってリグニンの話を直接お聞きするため三川先生を阪大にお訪ねしたことがあります。その頃“基礎木材工学”なる学生向け冊子を当時近畿大学で講義をもっていた 5 名の共著として執筆中であって、初版は昭和48 年に出版されました。従って三川先生にお会いしたのが 45-47 年の間と思います。既にその時、八浜先生の後任として阪大にきておられ、リグニン研究から離れて半導体をご研究中ということでしたが、実に懐かしそうにリグニンの話をされました。自らを誇るでなく、また惜しむ様子もなく一人の研究者として淡々と話された雰囲気がとても印象的でした。ただ繰り返し話された言葉は“リグニンは別れた女房のようなものだ。懐かしくもあり忘れ難い”と。東大理学部化学科卒の、いかにも秀才らしい、しかもえらぶった所のない紳士の面影が、育ちの良さとでもいえるのでしょうか、その柔和さと共に私にとって忘れられないリグニン化学者の一人です。

黎明期を便宜上昭和 30 年代と位置ずけると、私自身にとっても一つの転換期でした。恩師のお勧めを無げに断って大学を去り，通産省（当時）の工業試験所（いまの産総研）へ移ったのが昭和 37 年で、その主たる理由が十分な研究費を使って研究室をもちたいということでした。若気の至りという所でしたが、さて試験所で何をしたかということになると、これがリグニンのグラフト重合でした。時、恰も高分子全盛時代であって京大，阪大、阪市大などの工学系では物凄いブームで、高分子化学が跋扈した世の中でした。その時、工業技術院でも放射線の平和利用のための予算がつき、高分子センターになっていた大工試にガンマ線照射室が設けられることになった訳です。予算がついたから成果を出せという話になって、リグニンを基体とするグラフト重合を行うことを決めた訳です。今にして思えば、よくもまあ、やったものだという感がします。しかし、ガンマ線を使ったリグニンのグラフト重合は一つのアイデアだったかもしれないと今ではおもうのです。何故なら，リグニンは放射線に比較的強いからです。ただし、グラフトポリマーの物性に関する知識に乏しかったのが世に出なかった最大の理由だったと思います。放射線照射研究の場合、そのものが持つG_R 値、すなわち吸収エネルギー100e.V.当り生成するラジカル数が大きい意味をもちます。例えばメタクリル酸メチルはこの値が 6.3、スチレン

が 0.66、つまり芳香核など共鳴構造を多く持つものは放射線に強いことになります。この点から類推するとリグニンはかなり放射線に強くすぐに崩壊するセルロースとは対照的です。この特性を利用しリグニン-スチレングラフトポリマーをつくり、特性を調べると耐磨耗性は高く，半導体的性質も併せ持つことがわかりました。用いたリグニンは淡黄色の塩酸リグニンで研究用としては木粉から容易に製造できましたが、企業用原料としては当時適当とは言えず、また、放射線を使うことは設備、その他で制限を受けることになります。それでリグニン原料としては後述するようにパルプ廃液から得られるリグノスルホン酸がよく、レドックス開始グラフト重合が有望であることがわかりました。塩酸リグニンを用いるグラフト研究は昭和37-39年に行ったもので、リグノスルホン酸をベースにしたメタクリル酸メチルのグラフト研究は私が京大に移った為中断したのがいささか残念ではありました。昭和 39-41 年初頭まではシラキユウスのニューヨ-ク州立大学で働き、帰国後はリグニンとヘミセルロースの結合体、所謂LCCの研究に移りましたので、リグニンへのグラフト研究は終了しました。リグノスルホン酸にメタクリル酸メチルあるいはアクリロニトリルをレドックス系，例えば過酸化水素－第 1 鉄塩を開始剤としてグラフト重合させる反応は、前者は室温付近で、後者は零度でも進行する大変面白い反応なのでグラフトポリマーの物性を含めて、関心のある方は是非試してみる価値があると思っています。リグニン化学討論会は、後に化学系だけでなく生物系の研究者も加わってもらうため、東大での幹事会のとき中野先生らと話しあって“化学”を取り去り今のようにしたことを覚えています。このサロン的な集いが今後とも発展の原動力として存続することを願っています。

2005年、第50回討論会　特別寄稿

「第50回リグニン討論会を迎えて」

京都大学名誉教授（京都大学木質科学研究所）樋口隆昌

第50回リグニン討論会を迎えるにあたり、これまで、私達のグループが岐阜大学、京都大学で進めてきた、リグニンの生合成と微生物分解研究の流れと将来への展望に就いて簡単にまとめてみました。

私は1950年4月、岐阜大学農学部林学科木材化学講座（川村一次教授）の助手に採用されてから一貫してリグニンの生化学的研究を続けてきました。当時、欧米（Heidelberg, Prof. K. Freudenberg; Göteborg, Prof. E. Adler；Stockholm, Prof. H. Erdtman, Prof. E. Hägglund; Wien, Prof. K. Kratzl; Wisconsin, Prof. F.E. Brauns; New York, Prof. F.F. Nord; Toronto, Prof. H. Hibbert 等）では理学部、工学部関係の研究者が、主としてリグニンの化学構造、木材のパルプ蒸解と関連したリグニンの化学反応機構、リグニンの化学分解反応（ニトロベンゼン酸化、過マンガン酸酸化、エタノリシス、アシドリシス等）が研究されていました。更に1956年、A. Björkman によって milled wood lignin が調製され、リグニンの IR, UV スペクトル、分子量、上記した分解反応と分解生成物の解明が急速に進展しました。

しかし、リグニンは、タンパク質、セルロース、デンプンなど加水分解によって定量的に構成モノマーに分解される生体高分子と異なり、上記代表的な分解法でも分解生成物の収量は10—40％で、分解法によるリグニン化学構造の解明は不可能な特異な高分子である事が次第に明らかになってきました。

当時、我が国では、主としてリグニン研究に携わっておられた右田伸彦教授（東大農学部）、西田屹二教授（九大農学部）、館勇教授（京大農学部）、八浜義和教授（阪大工学部）の諸先生による協議の結果、第1回リグニン化学討論会が発足しました。その後、次第にリグニン研究の内要と分野が広くなり、現在のリグニン討論会に至っている。

私のリグニン研究は、そのような時期に始まりました。私は名大理学部生物学科（植物）の出身で、有機化合物の合成、反応解明、構造決定などの経験に乏しく、植物生化学の手法でリグニンの生化学的研究ができればと思っていましたので、リグニンの生合成に就いて研究を始める事にしました。その頃、八浜義和、岡部次郎：リグニン化学の最近の進歩（I）, (II). 化学の領域、南江堂、11, 1-12(1956), 12,15-31 (1956)が出版され、Freudenberg の研究室で、マッシュルーム酵素によるコニフェリルアルコールの脱水素重合で生成した、オリゴリグノール（グアイアシルグリセロール–β–コニフェリルエーテル、*d*,*l*-ピノレジノール、デヒドロジコニフェリルアルコール）と DHP の構造研究が詳細に紹介されました。

そこで手始めに Freudenberg の方法でマッシュルームのフェノールオキシダーゼを調製して酵素的性質を調べ、コニフェリルアルコールを脱水素重合させる酵素は CO 阻害を受けないラッカーゼ（*p*—ジフェノールオキシダーゼ）である事を突き止め、漆ラッカーゼとも比較した結果、樹木の木化（モノリグノールの脱水素重合）に関与する酵素は、ラッカーゼより、植物に一般的に分布しているペロキシダーゼである事を明らかにする事が出来ました。この結果（Biochemical studies of lignin formation (1), (2), (3). Physiol. Plantarum 10, 356, 621, 633 (1957); Further studies on phenol oxidase related to the lignin biosynthesis. J. Biochem. 45, 515 (1958) が Wien 大学の Prof. Kratzl の目にとまり、第4回国際生化学会（1958, Wien）で講演する機会を与えられたわけです。(T. Higuchi: Studies on the Biosynthesis of Lignin. pp161-188. Proc. 4th International Congress of Biochemistry 1958)

この学会で Prof. Freudenberg, Adler, Erdtman, Nord, Neish 等、それぞれの分野の代表的な研究者の研究発表と真剣な討論に接し、強い感銘を受けました。さらに学会後、ドイツ、スェーデンで各先生の研究室を訪問し、研究の実体を知る事が出来たのが、私の将来の研究方向を決定したように思います。

Dr. A.C. Neish（Prairie Regional Laboratory, Saskatoon, Canada）から同研究所の Dr. S. A. Brown がリグニンの生合成の研究を始めたので、一緒に研究をしませんかとお誘いをうけたのもこの学会でした。当時、岐阜大学ではアイソトープによるトレーサー実験は出来ませんでしたので、1960— 62の 2 年間、Saskatoon の平原地方研究所に滞在し、^{14}C-ラベルしたリグニン前駆物質（グルコース、シキミ酸、フェニルアラニン、ケイヒ酸、*p*-クマール酸、カフェー酸、フェルラ酸、シナピン酸など）を小麦植物体に投与して24時間代謝させてから、ニトロベンゼン酸化生成物（バニリン、シリンガアルデヒド）、エタノリシス生成物（ジケトン）の ^{14}C 活性を測定する方法で、モノリグノール生合成経路を解明していきました。その結果をとりまとめたのが、Dr. Brown と私によるモノリグノール生合成経路で、その後、内外の研究者によりモノリグノール生合成経路の基礎として引用されて来ています。

１９６８年、京都大学木材研究所に新設されたリグニン化学研究部門に招待され、島田幹夫（現京都大学名誉教授）、中坪文明（現京都大学教授）等の協力を得てリグニン生合成に関与する酵素（OMT 等）の解明、オリゴリグノールの合成、リグニンの微生物分解反応機構の解明等に力を入れてきました。

最近は研究法、分析法の進歩、関与する酵素の細胞内分布などが解明され、上記のモノリグノール生合成経路にバイパスや、一部改定が加えられていますが,我々のモノリグノール生合成経路の基本は、保たれていると思っています。

私の定年退職の頃からモノリグノール形成に関与する酵素の遺伝子解明が進み、最近ではポプラ、テーダ松、*Zinnia*、*Arabidopsis* などによる細胞壁合成に関する遺伝子と、その発現機構の解明（T. Higuchi, Pathways for monolignol biosynthesis via metabolic grids: coniferyl aldehyde 5-hydroxylase, a possible key enzyme in angiosperm syringyl lignin biosynthesis. Proc. Jpn. Acad., 79, 227-236. Ser B (2003) が進みつつあり、将来は利用目的と生態系に適した樹木の生産が可能になるものと考えられ、私達の研究がここまで発展してきている事を大変嬉しく思っています。

さらに私等はリグニンの微生物分解機構に就いても研究を進め、白色腐朽菌が分泌するリグニンペロキシダーゼ、ラッカーゼによって、リグニン側鎖ばかりで無く芳香環も分解される機構を ^{13}C, D, ^{18}O で標識したオリゴリグノール、DHP を基質として D_2O, $^{18}O_2$ の存在下でリグニンペロキシダーゼ分解し、分解生成物の分析によってそれらの分解機構を明らかにする事が出来ました。この研究分野も現在遺伝子レベルの研究に移行していますので、将来、バイオパルピングや生態環境浄化に繋がっていくものと期待しています（T. Higuchi, Microbial degradation of lignin : Role of lignin peroxidase, manganese peroxidase, and laccase. Proc. Jpn. Acad., 80, 204-214. Ser B(2004).

以上、私達がこれまでやってきたリグニンの生化学的研究についての経過と感想を思い出すままに記述しました。第５０回リグニン討論会に出席され、現在第一線でリグニンの研究に携わっておられる方々に少しでも参考になれば幸いです。今後、リグニン討論会のますますの発展を祈念しております。

第 1 回 (1956.11.12) 大阪、府立教育会館

1956-001
亜硫酸蒸解の速度を支配する因子について
坂田　功、千手諒一
九州大学大生産研究所
Factors controlling sulfite cooking rate
Isao Sakata, Ryoichi Senju
Institute of Industrial Science, Kyusyu University
Keywords: lignin sulfonic acid, delignification, sulfonation, successive reaction

1956-002
亜硫酸蒸解におけるフエノール成分の挙動
中野準三
東京大学農学部
Behavior of phenolic components during sulfite cooking
Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: Japanese red pine, *Pinus densiflora*, larch, *Larix Kaempferi*, pinosylvin, taxifolin, vanillyl alcohol, quercetin

1956-003
落葉樹のサルファイト蒸解について
軒原栄三
国策パルプ株式会社
Sulfite cooking of larch
Eizo Nokihara
Kokusaku Pulp Co., Ltd.
Keywords: heartwood, sapwood, taxifolin,ε-galactan

1956-004
クラフト蒸解機構
三川　礼
国策パルプ株式会社
Mechanism of kraft cooking
Rei Mikawa
Kokusaku Pulp Co., Ltd.
Keywords: lignin, sodium sulfide, mercaptan, monosulfide, disulfide, X-group, Z-group, B-group

1956-005
リグノスルホン酸中の酸性基について（第一報）
佐藤孝一
国策パルプ株式会社
Acidic groups in lignosulfonic acid (I)
Koichiro Sato
Kokusaku Pulp Co., Ltd.
Keywords: sulfonic acid group, carboxylic acid group, guaiacyl-type, phenolic hydroxyl group, condensed phenolic hydroxyl group, X-group, Z-group, B-group

1956-006
リグノスルホン酸の鞣皮性と多分子性
京極与寿郎、八浜義和
大阪大学工学部

Tannability and multimolecularity of lignosulfonic acid
Yojuro Kyogoku, Yoshikazu Hachihama
Faculty of Engineering, Osaka University
Keywords: degree of sulfonation, tannability, multimolecularity

1956-007
幼植物のリグニン形成について
石川久雄、高市克美、喜多川重樹、沖　妙
愛媛大学農学部
Formation of lignin in juvenile plant
Hisao Ishikawa, Katumi Takaiti, Sigeki Kitagawa, Tae Oki
Faculty of Agriculture, Ehime University
Keywords: shikimic acid, phenylalanine, tyrosine, coniferin, syringin, coniferyl alcohol, peroxidase, mung bean, *Robinia pseudoacacia*,

1956-008
植物体中におけるリグニンの形成機構
樋口隆昌、川村一次
岐阜大学農学部
Formation mechanism of lignin in plant
Takayoshi Higuchi, Ichiji Kawamura
Faculty of Agriculture, Gifu University
Keywords: phenylalanine, coniferin, β-glucosidase, coniferyl alcohol, peroxidase, laccase

1956-009
リグニンの呈色機構に関する研究
右田伸彦、中野準三、平川公夫
東京大学農学部
On the mechanism of color reaction of lignin
Nobuhiko Migita, Junzo Nakano, Kimio Hirakawa
Faculty of Agriculture, the University of Tokyo
Keywords: Mäule color reaction, Cross-Bevan color reaction, phloroglucinol-hydrochloric acid color reaction

1956-010
リグニンの呈色について
中村徳郎[*1]、北浦貞男[*2]
[*1]興国人絹パルプ株式会社、[*2]九州大学生産研究所
On the color reaction of lignin
Tokurou Nakamura[*1], Sadao Kitaura[*2]
[*1]Koukoku Jinken Pulp Co. Ltd. [*2] Institute of Industrial Science, Kyusyu University
Keywords: chromopholic group, coniferaldehyde, Schiff's reagent

1956-011
リグニンの水添分解に関する研究
榊原　彰、荒木　正
林業試験場
Hydrogenolysis of lignin
Akira Sakakibara, Tadasi Araki
Forestry and Forest Product Research Institute
Keywords: hydrogenolysis, residual lignin from wood saccharification, sulfite spent liquor

1956-012
リグニンに関する研究（第 3 報）低スルホン化木紛のエタノリシスについて

石原達夫、近藤民雄
林業試験場
Studies on lignin (III), Ethanolysis of sulfonated wood meal
Tatsuo Ishihara, Tamio Kondo
Forestry and Forest Product Research Institute
Keywords: ethanolysis, Hibbert's ketones, guaiacylglycerol, structure moiety A by Erdtman

1956-013
リグニンの分解に関する研究（第 1 報）ニトロベンゼン酸化生成物について
田中次郎、近藤民雄
林業試験場
Studies on degradation of lignin (I), Nitrobenzene oxidation products
Jiro Tanaka, Tamio Kondo
Forestry and Forest Product Research Institute
Keywords: vanillin, paperchromatography, quantitative determination by UV absorption

1956-014
木材糖化リグニンの性状（続）
岡部次郎、八浜義和
大阪大学工学部
Properties of residual lignin from wood saccharification
Jiro Okabe, Yoshikazu Hachihama
Department of Engineering, Osaka University
Keywords: nitrobenzene oxidation, Klason lignin, vanillin

1956-015
竹リグニンの研究
大野一月、三浦克己
大阪府立大学工学部
Studies on bamboo lignin
Kazuki Ono, Katsumi Miura
Department of Engineering, Osaka Prefectural University
Keywords: nitrobenzene oxidation, paper chromatography, kraft cooking

1956-016
リグニン多糖類複合体とパルプ原木の近似組成の関係
本田真一
浜松商科短期大学
Similarity in composition between pulp wood and lignin-carbohydrate complex
Shinichi Honda
Hamamatsu Commercial College
Keywords: hardwood, conifer, furfural, pentose

第 2 回 (1957.11.15) 東京、紙パルプ会館

1957-001
幼植物のリグニン形成について（第 8 報）
石川久雄、高市克美、沖　妙
愛媛大学農学部
Formation of lignin in juvenile plant (VIII)
Hisao Ishikawa, Katsumi Takaichi, Tae Oki
Faculty of Agriculture, Ehime University
Keywords: aromatic amino acid, tannin, shikimic acid, phenylalanine, tyrosine

1957-002
コニフェリールアルコール重合に関与するフェノールオキシダーゼについて
樋口隆昌、川村一次、井藤佳美
岐阜大学農学部
On the phenol oxidase responsible for polymerization of coniferyl alcohol
Takayoshi Higuchi, Ichiji Kawamura, Yosimi Ito
Faculty of Agriculture, Gifu University
Keywords: laccase, peroxidase, tyrosinase, dehydrogenative polymerization

1957-003
リグニンと炭水化物との化学結合に関する研究（第 5 報）小麦藁中におけるフェノールグルコサイド結合の存在について
林　晄、 館　勇
京都大学農学部
Studies on the chemical linkages between lignin and carbohydrates (V), Presence of phenylglucoside bonds in wheat straw
Akira Hayashi, Isamu Tachi
Faculty of Agriculture, Kyoto University
Keywords: acetylated xylolignin, dioxane lignin, UV spectra

1957-004
樹皮のリグニンについて
幡　克美、十河村男
香川大学農学部
On lignin in bark
Katsumi Hata, Murao Sogo
Faculty of Agriculture, Kagawa University
Keywords: dioxane lignin, Willstätter lignin, nitrobenzene oxidation, *Pinus densiflora*,

1957-005
消石灰による S.P.廃液中の L.S.の沈澱について
北浦貞男、上野雄造
九州大学農学部
On the precipitation of lignosulfonic acid by calcium hydroxide from sulfite spent liquor
Sadao Kitaura, Yuzo Ueno
Faculty of Agriculture, Kyusyu University
Keywords: carbohydrates, glucose, mannose, galactose, arabinose, xylose

1957-006
リグニンスルホン酸の沈降恒数の測定
京極与寿郎、八浜義和
大阪大学工学部
Determination of sedimentation coefficient of lignosulfonic acid

Yoshiro Kyogoku, Yoshikazu Hachihama
Faculty of Engineering, Osaka university
Keywords: molecular weight, diffusion coefficient, sulfite spent liquor

1957-007
赤外線吸収スペクトルによるリグニンの研究
祖父江寛、福原節雄
東京大学工学部
Studies on lignin by infrared spectroscopy
Hiroshi Sobue, Setsuo Fukuhara
Faculty of Engineering, the University of Tokyo
Keywords: Brauns's native lignin, beech, *Picea jezoensis*, spruce, *Cryptomeria japonica*, holocellulose

1957-008
リグニンのベンジルアルコール性 OH 基の新反応と考えられるチオ尿素とリグニンとの反応について
三川 礼
国策パルプ株式会社
Reaction of lignin with thiourea – A new reaction of benzyl alcoholic hydroxyl group in lignin
Rei Mikawa
Kokusaku Pulp Co., Ltd.
Keywords: lignin, thiourea, benzyl alcoholic hydroxyl group, X-group, Z-group

1957-009
リグニンモデル化合物の硫化に関する研究
石原達夫、近藤民雄
林業試験場
Studies on the reaction of lignin model compounds with hydrogen sulfide
Tatsuo Ishihara, Tamio Kondo
Forestry and Forest Product Research Institute
Keywords: hydrogen sulfide, benzyl alcohol, benzyl ether, thioxane

1957-010
ベンジルグループの hydrogenolysis
右田伸彦、中野準三、石津 敦
東京大学農学部
Hydrogenolysis of benzyl group
Nobuhiko Migita, Junzo Nakano, Atsushi Ishizu
Faculty of Agriculture, the University of Tokyo
Keywords: benzyl alcohol, benzyl ether, aromatic hydroxyl group, methanol lignin

1957-011
リグニンの臭素化について
北浦貞男、中村徳郎
九州大学農学部
On the bromination of lignin
Sadao Kitaura, Tokurou Nakamura
Faculty of Agriculture, Kyusyu University
Keywords: *Abies sachaliensis,* substitution reaction, lignin model compounds, native lignin

1957-012
パルプ漂白の際のリグニンの挙動について
佐藤孝一郎、海老沢きよ
国策パルプ株式会社
Behavior of lignin during bleaching of pulp

Koichiro Sato, Kiyo Ebisawa
Kokusaku Pulp Co., Ltd.
Keywords: bleaching, chlorination, lignosulfonic acid, hydrochlonic acid lignin, thiolignin, carbonyl group

1957-013
ハドロトロピック塩による脱リグニン
右田伸彦、中野準三
東京大学農学部
Delignification by hydrotropic salt
Nobuhiko Migita, Junzo Nakano, Atsushi Ishizu
Faculty of Agriculture, the University of Tokyo
Keywords: beech, sodium xylenesulfonate, semichemical pulp, dissolving kraft pulp, kraft pulp

1957-014
ハドロトロピックリグニンの酸化
万木　正、鈴木英吉
繊維工業試験所
Oxidation of hydrotropic lignin
Tadashi Yurugi, Eikichi Suzuki
Institute of Fiber Science and Technology
Keywords: beech, nitrobenzene oxidation, guaiacyl group, syringyl group.

1957-015
広葉樹リグニンのニトロベンゼン酸化生成物
田中次郎、近藤民雄
林業試験場
Nitrobenzene oxidation products from hardwood lignin
Jiro Tanaka, Tamio Kondo
Forestry and Forest Product Research Institute
Keywords: beech, condensed structure, dehydrodivanillin

1957-016
リグニンの水素添加分解物の硝酸酸化
岡部次郎[*1], 八浜義和[*2]
[*1] 山陽パルプ, [*2] 阪大工
Nitric acid oxidation of hydrocracking products of lignin
Jiro Okabe[*1], Yoshikazu Hachihama[*2]
[*1]Sanyo Pulp Co., Ltd., [*2] Faculty of Engineering, Osaka University
Keywords: lignin, hydrogenolysis, Nitric acid oxidation, adipic acid

1957-017
鞣剤としてのリグニンスルホン酸
千手諒一
九州大学農学部
Lignin sulfonic acid as a tanning agent
Ryoichi Senju
Faculty of Agriculture, Kyusyu University
Keywords: plant tannin, adsorption of tanning agent, diffusion of tanning agent

1957-018
リグニンスルホン酸の酸化
祖父江寛、斉藤吉民
東京大学工学部
Oxidation of lignosulfonic acid

Hiroshi Sobue, Yoshitami Saito
Faculty of Engineering, the University of Tokyo
Keywords: sulfite spent liquor, oxidation by sodium hydroxide, vanillin

1957-019
バニリンより高分子化合物の合成に関する研究
舘　勇、村上浩二
京都大学農学部
Studies on the synthesis of macromolecular compounds from vanillin
Isamu Tachi, Koji Murakami
Faculty of Agriculture, Kyoto University
Keywords: polyurethane, polyamide urethane, polyester

1957-020
6（及び7-）-カルボキシ-2-ヒドロキシメチル-1,4-ベンゾジオキサンより生成するポリエステル繊維の製造研究
万木　正、長谷川正木
繊維工業試験場
Production of polyester fiber from 6-(or 7-)-carboxy-2-hydroxymethyl-1,4-benzodioxane
Tadashi Yurugi, Masaki Hasegawa
Institute of Fiber Science and Technology
Keywords: protocatechuic acid, epichlorohydrin

第3回 (1958.11.04) 九州大学農学部

1958-001
プロトリグニンの臭素化について
中村徳郎、北浦貞男
九州大学農学部
On the bromination of protolignin
Tokurou Nakamura, Sadao Kitaura
Faculty of Agriculture, Kyusyuu University
Keywords: *Abies sachaliensis,* lignin model compound, dehydrogenative polymer, urushi laccase

1958-002
リグニンの生成母体の生成に関する研究
石川久雄、沖 妙
愛媛大学農学部
Studies on the biosyntheses of lignin precursors
Hisao Ishikawa, Tae Oki
Faculty of Agriculture, Ehime University
Keywords: biosynthesis, shikimic acid, phenylalanine, tyrosine, gallotannin

1958-003
幼植物のリグニンについて
川村一次
岐阜大学農学部
On the lignin in juvenile plant
Ichiji Kawamura
Faculty of Agriculture, Gifu University
Keywords: *Pinus Thunbergii*, *Robinia pseudoacacia*, guaiacyl nucleus, syringyl nucleus, methoxyl content

1958-004
リグニンと炭水化物との化学結合に関する研究（第 6 報）小麦藁のジメチルホルムアミド抽出物について
林 晄、 館 勇
京都大学農学部
Studies on the chemical bond between lignin and carbohydrates (VI), Dimethylformamide extracts from wheat straw
Akira Hayashi, Isamu Tachi
Faculty of Agriculture, Kyoto University
Keywords: lignin-carbohydrate complex, milled wood lignin,

1958-005
針葉樹及び広葉樹に生育した寄生木（やどりぎ）のリグニンについて
中島浩二、八浜義和、F.E. Brauns
大阪大学工学部
On the lignin of mistletoe grown on coniferous trees and broad-leaved trees
Koji Nakajima, Yoshikazu Hachihama, F.E. Brauns
Faculty of Engineering, Osaka University
Keywords: *Quercus* sp., *Pinus ponderosa*, *Mistletoe pholadendron flavescens*, Mäule color reaction, thioglycolic acid lignin, ethanolysis

1958-006
Lignum Vitae 中のリグニンについて
中島浩二、八浜義和、F.E. Brauns
大阪大学工学部
On the lignin in lignum vitae

Koji Nakajima, Yoshikazu Hachihama, F.E. Brauns
Faculty of Engineering, Osaka University
Keywords: *Guaiacum officinale*, methoxyl content, Mäule color reaction

1958-007
リグニンスルホン酸の高分子化学的性状について
京極与寿郎、八浜義和
大阪大学工学部
Macromolecular properties of lignin sulfonic acid
Yoshiro Kyougoku, Yoshikazu Hachihama
Faculty of Engineering, Osaka University
Keywords: polymolecularity, ion-exchange resin chromatography

1958-008
リグニンのエステルグループ
中野準三、石津　敦、右田伸彦
東京大学農学部
Ester group in lignin
Junzo Nakano, Atsushi Ishizu, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: *p*-hydroxybenzoic acid, vanillic acid, syringic acid, *p*-coumaric acid, ferulic acid, *Populus Sieboldii*, *Populus Maximowiczii*

1958-009
リグニンとメルカプタンの反応
石原達夫、近藤民雄
林業試験場
Reaction of mercaptan with lignin
Tatsuo Ishihara, Tamio Kondo
Forestry and Forest Product Research Institute
Keywords: hydrogen sufide, ethyl mercaptan, vanillyl alcohol, mercaptolysis

1958-010
広葉樹リグニンのアルカリ分解
田中次郎、近藤民雄
林業試験場
Degradation of hardwood lignin by sodium hydroxide
Jiro Tanaka, Tamio Kondo
Forestry and Forest Product Research Institute
Keywords: beech, sodium hydroxide, 4,4’-dihydroxy-3,3’-dimethoxystilben

1958-011
S.P.廃液のアルカリ溶液に於ける酸化について
舘　勇、浦野信清、赤嶋晋一郎、山本昭
京都大学農学部
Oxidation of sulfite spent liquor in alkaline medium
Isamu Tachi, Nobukiyo Urano, Sinichiro Akashima, Akira Yamamoto
Faculty of Agriculture, Kyoto University
Keywords: vanillin, vanillic acid, yield of vanillin

1958-012
バニリンより高分子化合物の合成に関する研究- β-ヒドロキシエトキシ-バニリン酸のポリエステルの性状について
舘　勇、村上浩二

京都大学農学部
Studies on the synthesis of macromolecular compounds from vanillin- On the properties of polyester prepared fromβ-hydroxyethoxy-vanillic acid
Isamu Tachi, Koji Murakami
Faculty of Agriculture, Kyoto University
Keywords: transesterification, catalyst, infrared spectrum

1958-013
バニリン酸誘導体の合成とその高分子物質への応用
長谷川正木
繊維工業試験場
Synthesis of vanillin derivatives and their use for polymer production
Masaki Hasegawa
Institute of Fiber Science and Technology
Keywords: vanillin, vanillic acid, epichlorohydrin, hexamethylene diamine

1958-014
アルカリ性亜硫酸ソーダ蒸解について
坂田 功、千手諒一
九州大学農学部
On the alkaline sulfite cooking
Isao Sakata, Ryoichi Senjyu
Faculty of Agriculture, Kyusyu University
Keywords: *Castanopsis* sp., sulfonation, delignification

1958-015
未晒パルプより抽出されるリグニンの量的関係
佐藤孝一郎，三川 礼
国策パルプ株式会社
Amount of lignin extracted from unbleached pulps
Koichiro Sato, Rei Mikawa
Kokusaku Pulp Co., Ltd.
Keywords: unbleached pulp, beating, dimethysulfoxide, extraction, lignin, lignin-carbohydrate complex

第 4 回 (1959.11.13-14) 京大、楽友会館

1959-001
リグニンの生合成に関する研究— ユウガオ果実の木質化に関与する酵素と有機酸の消長について
館 勇、佐藤 惺
京都大学農学部
Studies on the biosynthesis of lignin – Changes in content of enzymes and organic acids related to lignification of kanpyo, a fruit of *Lagenaria siceraria* var. *hispida*
Isamu Tachi, Satoru Sato
Faculty of Agriculture, Kyoto University
Keywords: laccase, peroxidase, shikimic acid, quinic acid

1959-002
^{14}C−アイソトープに依るリグニン生合成の研究
長谷川正男＊[1]、樋口隆昌＊[2]
＊[1]林業試験場、＊[2]岐阜大学農学部
Studies on the biosynthesis of lignin using ^{14}C-isotope
Masao Hasegawa, Takayoshi Higuchi
＊[1]Forestry and Forest Product Research Institute,＊[2]Faculty of Agriculture, Gifu University
Keywords: phenylpropane, shikimic acid, protocatechuic acid, dehydroshikimic acid

1959-003
リグニン生成母体の形成について
石川久雄、沖 妙
愛媛大学農学部
On the biosyntheses of lignin precursors
Hisao Ishikawa, Tae Oki
Faculty of Agriculture, Ehime University
Keywords: *Bacillus cereus*, dehydroshikimic acid, protocatechuic acid, aromatic amino acids

1959-004
ミズナラ樹皮のリグニンについて
幡 克実、十河村男
香川大学農学部
On the lignin in the bark of Japanese oak (*Quecus cryspura*)
Katsumi Hata, Murao Sogo
Faculty of Agriculture, Kagawa University
Keywords: dioxane lignin, hydrochloric acid lignin, UV spectra, IR spectra

1959-005
下等植物のリグニンについて（第一報）ヘゴ及びコフキサルノコシカケのリグニン
川村一次、樋口隆昌、近藤雅春
岐阜大学農学部
On the lignin of lower plants. I. Lignin in *Cythea spinulosa* and *Fomea applanatus*.
Ichiji Kawamura,Takayoshi Higuchi, Masaharu Kondo
Faculty of Agriculture, Gifu University
Keywords: wood rotting fungi, color reaction, Klason lignin, dioxane lignin, nitrobenzene oxidation

1959-006
リグニンと炭水化物との化学結合に関する研究
林 晄、 館 勇
京都大学農学部
Studies on the chemical linkages between lignin and carbohydrates
Faculty of Agriculture, Kyoto University

Akira Hayashi, Isamu Tachi
Keywords: wheat straw, lignin-carbohydrate complex, sugar composition

1959-007
酢化した木材粉とエチレンオキサイドの反応について
石川久雄、山下謙三
愛媛大学農学部
On the reaction of ethylene oxide with acetylated wood meal
Hisao Ishikawa, Kenzo Yamashita
Faculty of Agriculture, Kagawa University
Keywords: beech, hydroxyethyl lignin, hydroxyethyl cellulose, Brauns's native lignin

1959-008
リグニンの単離及びリグニンの反応性について
福渡七郎、竹田貴美、宮崎親二郎
島根農科大学
On the isolation of lignins and their reactivity
Shichiro Fukuwatari, Takami Takeda, Sinjiro Miyazaki
Shimane Agricultural University
Keywords: kraft lignin, lignosufonic acid, Purves lignin, γ-ray irradiated lignin

1959-009
脱リグニン反応とその過程について
福渡七郎、安田徳郎、石野荘造、柳浦千里
島根農科大学
On the delignification reaction and its process
Shichiro Fukuwatari, Tokuro Yasuda, Shozo Ishino, Chisato Yagiura
Shimane Agricultural University
Keywords: chlorination, holocellulose, *Tilia japonica, Pinus densiflora, Eucalyptus, Populus Sieboldii, Quercus crispula*

1959-010
リグニンスルホン酸に関する研究（第一報）
舘　勇[*1]、林　晄[*1]、小島義一[*2]、東辻　健[*2]
[*1] 京都大学農学部、[*2]丸菱油脂工業株式会社
Studies on the lignin sulfonic acid (I)
Isamu Tachi[*1], Akira Hayashi[*1], Giichi Kojima[*2], Ken Higashitsuji[*2]
[*1]Faculty of Agriculture, Kyoto University, [*2]Marubishi Oil and Fat Co. Ltd.
Keywords: sulfite waste liquor, separation by extraction, dicyclohexylamine salt

1959-011
リグニンスルホン酸に関する研究（第二報）
舘　勇[*1]、林　晄[*1]、小島義一[*2]、東辻　健[*2]
[*1] 京都大学農学部、[*2]丸菱油脂工業株式会社
Studies on the lignin sulfonic acid (II)
Isamu Tachi[*1], Akira Hayashi[*1], Giichi Kojima[*2], Ken Higashitsuji[*2]
[*1]Faculty of Agriculture, Kyoto University, [*2]Marubishi Oil and Fat Co. Ltd.
Keywords: molecular weight, melting point depression method, ethylene carbonate

1959-012
未晒パルプよりジメチルスルホオキサイド抽出した成分について
佐藤孝一郎，小林晃夫
国策パルプ株式会社
Component of dimethysulfoxide extract of unbleached pulps

Koichiro Sato, Akio Kobayashi
Kokusaku Pulp Co., Ltd.
Keywords: beating, extraction, lignin, lignin-carbohydrate complex

1959-013
未晒 SP より抽出したリグニンスルホン酸の分子量について
佐藤孝一郎，小林晃夫，三川　礼
国策パルプ株式会社
Molecular weight of lignin sulfonic acid extracted from unbleached sulfite pulp
Koichiro Sato, Akio Kobayashi, Rei Mikawa
Kokusaku Pulp Co., Ltd.
Keywords: dimethysulfoxide, extraction, lignosulfonic acid

1959-014
リグニンの物理化学的研究（第 1 報）微分容量より見たリグニンスルホン酸塩の一考察
上田静男、辻　福寿、林　晄、渡辺　昌、中井章能
京都大学農学部
Physicochemical studies on ligninc Differential capacity of lignosulfonate
Shizuo Ueda, Fukujyu Tsuji, Akira Hayashi, Akira Watanabe, Akiyoshi Nakai
Faculty of Agriculture, Kyoto University
Keywords: dropping mercury electrode, electrical double layer, surface active property

1959-015
リグニンの物理化学的研究（第 2 報）微分容量より見たリグニンスルホン酸塩の一考察
上田静男、辻　福寿、林　晄、渡辺　昌、中井章能
京都大学農学部
Physicochemical studies on lignin (I), Differential capacity of lignosulfonate
Shizuo Ueda, Fukujyu Tsuji, Akira Hayashi, Akira Watanabe, Akiyoshi Nakai
Faculty of Agriculture, Kyoto University
Keywords: electric frequency

1959-016
チオリグニンのポーラログラフィー（第 7 報〉 接触波の活性基について（I）
神田　孝、寺島典二、川上日出国
名古屋大学農学部
Polarography of lignin（VII）, On the active group of thiolignin catalytic wave (1)
Takashi Kanda, Noritsugu Terashima, Hidekuni Kawakami
Faculty of Agriculture, Nagoya University
Keywords: *Pinus densiflora*, reduction, sodium borohydride, Raney nickel

1959-017
ニトロリグニンのポーラログラフィー
永田美之介、北尾弘一郎、舘　勇
京都大学農学部
Polarography of nitrolignin
Yoshinosuke Nagata, Kouichiro Kitao, Isamu Tachi
Faculty of Agriculture, Kyoto University
Keywords: m-nitrophenol, low molecular nitrocompounds

1959-018
Vanillin より高分子化合物の合成に関する研究（第４報）
村上浩二、舘　勇
京都大学農学部
Studies on the synthesis of high polymer from vanillin (IV)

Koji Murakami, Isamu Tachi
Faculty of Agriculture, Kyoto University
Keywords: vanillic acid, polyamide, solubility

1959-019
リグニンとメルカプタンとの反応
石原達夫
林業試験場
Reaction of lignin and mercaptan
Tatsuo Ishihara
Forestry and Forest Product Research Institute
Keywords: mercaptolysis, ethyl mercaptan, mercaptol, lignin model compounds

1959-020
リグニンの臭素化について
中村徳郎、北浦貞夫
九州大学農学部
On the bromination of lignin
Tokurou Nakamura, Sadao Kitaura
Faculty of Agriculture, Kyusyu University
Keywords: protolignin, sodiumborohydride

1959-021
アルカリリグニンのα位にカルポニル基をもつた側鎖構造について
右田伸彦、石津　敦
東京大学農学部
On the α-carbonyl side chain structure in alkali lignin
Nobuhiko Migita, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: condensation, acetovanillone, propiovanillone, 3,4-dihydroxypropiovanillone

1959-022
広葉樹リグニンの分解生成物について
田中治郎
林業試験場
On the alkali degradation products of hardwood lignin
Jiro Tanaka
Forestry and Forest Product Research Institute
Keywords: beech, alkali degradation, syringyl ethane

1959-023
バニリンの酸素酸化について
舘　勇、村上浩二、阿部圭二
京都大学農学部
On the oxidation of vanillin with oxygen
Isamu Tachi, Koji Murakami, Keiji Abe
Faculty of Agriculture, Kyoto University
Keywords: oxidation with oxygen, UV absorption spectrum

1959-024
リグニンとフエノールスルホン酸の反応
中島浩二[*1]、八浜義和[*2]
[*1] 山陽パルプ株式会社、[*2] 大阪大学工学部
Reaction of lignin with phenol sulfonic acid

Koji Nakajima[*1] , Yoshikazu Hachihama[*2]
[*1]Sanyo Pulp Co. Ltd, [*2]Faculty of Engineering, Osaka University
Keywords: Brauns's native lignin, condensation, Japanese red pine

1959-025
高分子凝集剤によるリグニンの沈澱（第 2 報）
佐々木壮吉
東京工業試験所
Precipitation of lignin by polymer flocculant (II)
Sokichi Sasaki
The Government Chemical Industrial Research Institute, Tokyo
Keywords: sulfite waste liquor, dicyanodiamide, formalin, semichemical pulp waste liquor

1959-026
広葉樹リグニンスルホン酸に関する研究
京極与寿郎、位田博敏、八浜義和
大阪大学工学部
Studies on the hardwood lignin sulfonic acid
Yoshiro Kyogoku, Hirotoshi Ida, Yoshikazu Hachihama
Faculty of Engineering, Osaka University
Keywords: beech, heterogeneity, polymolecularity, nitrobenzene oxidation

1959-027
リグニンの利用に関する研究
舘 勇、林 晄、山本 昭
京都大学農学部
Studies on the utilization of lignin
Isamu Tachi, Akira Hayashi, Akira Yamamoto
Faculty of Agriculture, Kyoto University
Keywords: tanning agent, lignin sulfonic acid, oxidized lignin sulfonic acid

1959-028
リグニン及び木材に対する放射線の作用
高椋節夫、八浜義和
大阪大学工学部
Effect of radiation on lignin and wood
Setsuo Takamuku, Yashikazu Hachihama
Faculty of Engineering, Osaka University
Keywords: Japanese red pine, spruce, cobalt 60, Brauns's native lignin, infrared spectrometry

1959-029
リグニンに対する放射線照射効果
祖父江寛, 上埜武夫
日本放射線高分子研究協会
Effect of radiation on lignin
Hiroshi Sobue, Takeo Ueno
Japan Radiation Polymer Research Association
Keywords: γ-ray, irradiation, paramagnetic resonance spectroscopy, free radical

第5回 (1960.11.19-20) 名古屋、商工会議所

1960-001
リグニンの高圧水素添加分解
鹿島　覚、長田　武、田畑晴朗、渡辺　浩、久保輝雄
野口研究所
Hydrocracking of lignin
Satoru Kashima, Takeshi Nagata, Haruo Tabata, Hiroshi Watanabe, Teruo Kubo
Noguchi Institute
Keywords: liquefaction rate, *p*-cresol, 4-ethylphenol, pyrocatechol

1960-002
リグニンの高圧水添分解に関する研究
榊原　彰、荒木　正
林業試験場
Studies on the hydrogenolysis of lignin
Akira Sakakibara, Tadashi Araki
Forestry and Forest Product Research Institute
Keywords: phenol, cresols, catechols, xylenols, ethylphenol

1960-003
リグニンスルホン酸に関する研究（VII) 水溶液の電導度並びに拡散係数について
小島義一、中井章能、舘　勇
京都大学農学部
Studies on the lignin sulfonic acid. VII. Electric conductivity and diffusion coefficient of the aqueous solution
Giichi Kojima, Akiyosi Nakai, Isamu Tachi
Faculty of Agriculture, Kyoto University
Keywords: electric conductivity, diffusion coefficient, micelle formation, association

1960-004
リグニンスルホン酸に関する研究（VIII） 非水溶媒中による分別
小島義一、東辻　健、林　晄、舘　勇
京都大学農学部
Studies on the lignin sulfonic acid (VIII), Fractionation by nonaqueous solvents
Gi-ichi Kojima, Ken Azumatsuji, Akira Hayashi, Isamu Tachi
Faculty of Agriculture, Kyoto University
Keywords: dicyclohexylamine salt, molecular weight, fractional precipitation, molecular weight

1960-005
リグニンスルホン酸に関する研究（IX）非水溶媒中における粒度の測定
小島義一、林　晄、舘　勇
京都大学農学部
Studies on the lignin sulfonic acid (IX), Determination of particle size in nonaqueous solvents
Gi-ichi Kojima, Akira Hayashi, Isamu Tachi
Faculty of Agriculture, Kyoto University
Keywords: dicyclohexylamine salt, dicyclohexylamine hydrochloric acid salt, dissociation

1960-006
光散乱法によるリグニンスルホン酸塩の研究
鈴木　勇[*1]，京極与寿郎[*2]，八浜義和[*2]
[*1] 国策パルプ株式会社，[*2] 大阪大学工学部
Studies on light scattering spectrophotometry of lignosulfonate
Isamu Suzuki[*1], Yoshiro Kyogoku[*2], Yoshikazu Hachihama[*2]
[*1]Kokusaku Pulp Co., Ltd., [*2]Osaka University, Faculty of Technology

Keywords:	light scattering spectrophotometry, lignosulfonate, molecular weight

1960-007
リグニンの物理化学的研究（第 3 報）
上田静男、渡辺　昌、辻　福寿
京都大学化研究所
Physicochemical study of lignin (III)
Shizuo Ueda, Akira Watanabe, Fukutoshi Tsuji
Institute for Chemical Research, Kyoto University
Keywords:	electric conductivity, micelle formation, molecular weight

1960-008
リグニンのポーラログラフイー（第 9 報）接触波の活性基について（3）
神田　孝、寺島典二、川上日出国
名古屋大学農学部
Polarography of lignin (IX) On the active group of thiolignin catalytic wave (3)
Takashi Kanda, NoritsuguTerashima, Hidekuni Kawakami
Faculty of Agriculture, Gifu University
Keywords:	thiolignin, sodalignin, lignin model compounds, carbonyl group

1960-009
ナギ、ラカンマキ及びイチョウ材のリグニンについて
川村一次、樋口隆昌
岐阜大学農学部
On the lignin in *Podocarpus nagi*, *Podocarpus chinensis* and *Ginkgo biloba*
Ichiji Kawamura, Takayoshi Higuchi
Faculty of Agriculture, Gifu University
Keywords:	Mäule color reaction, nitrobenzene oxidation, milled wood lignin, UV absorption spectrum, IR absorption spectrum

1960-010
アカマツ樹皮フエノール酸の性状
幡　克美、十河村男
香川大学農学部
Properties of phenolic acids in the bark of red pine
Katsumi Hata, Murao Sogo
Faculty of Agriculture, Kagawa University
Keywords:	ethanolysis, protocatechualdehyde, methoxyl group content

1960-011
リグニンと炭水化物との化学結合に関する研究
林　晄
立命館大学理工学部
Studies on the chemical bonds between lignin and carbohydrates
Akira Hayashi
College of Science and Engineering, Ritsumeikan University
Keywords:	DMF extractives, phenol glucoside bond, uronic acid ester bond

1960-012
リグニンの単離及び反応性について（II）フエノール及びアニリンとの結合反応について
福渡七郎、渡辺　寿、安田徳郎
島根農科大学
On isolation and reactivity of lignin (II), Reaction with phenol and anilin
Hichirou Fukuwatari, Hisashi Watanabe, Tokurou Yasuda

Shimane University of Agriculture
Keywords: soda pulp lignin, sulfate pulp lignin, sulfuric acid lignin, γ-ray lignin

1960-013
グアヤコールの塩素水による塩素化について
佐藤孝一郎，小林晃夫，三川　礼
国策パルプ株式会社
Chlorination of guaiacol with aqueous chlorine solution
Koichiro Sato, Akio Kobayashi, Rei Mikawa
Kokusaku Pulp Co., Ltd.
Keywords: guaiacol, aqueous chlorine solution, chlorination, methoxyl group, methanol

1960-014
リグニン中のフエノール性水酸基のヒドロオキシエチル化について
石川久雄、沖　妙
愛媛大学農学部
On the hydroxyethylation of phenolic hydroxyl groups in lignin
Hisao Ishikawa, Tae Oki,
Faculty of Agriculture, Ehime University
Keywords: beech, neutral sulfite pulping, guaiacyl-syringyl lignin, UV spectrum

1960-015
芳香核カルポン酸形成に関与する酵素系について
石川久雄、沖　妙
愛媛大学農学部
On the enzymes participate in formation of aromatic carboxylic acids
Hisao Ishikawa, Tae Oki,
Faculty of Agriculture, Ehime University
Keywords: *Bacillus cereus*, shikimic acid, 5-dehydroshikimic acid, dehydroshikimic acid dehydrase

1960-016
リグニンの生合成に関する研究、 ユウガオ果実の木質化に関与する酵素とコニフェリルアルコールの酸化について
佐藤　惺、舘　勇
京都大学農学部
Studies on the biosynthesis of lignin. Enzymes related to lignification of kanpyo, a fruit of *Lagenaria siceraria* var. *hispida* and oxidation of coniferyl alcohol
Akira Sato, Isamu Tachi
Faculty of Agriculture, Kyoto University
Keywords: laccase, peroxidase, dehydrogenative polymerization products (DHP)

1960-017
過酸化物によるリグニンの酸化
尾上史郎，大久保正道，池田健郎
山陽パルプ株式会社
Oxidation of lignin with peroxides.
Shiro Onoe, Masamichi Okubo, Kenro Ikeda
Sanyo Pulp Co., Ltd.
Keywords: sulfite pulp, lignin, peroxide, barium peroxide, oxidation, vanillin, vanillic acid

1960-018
過マンガン酸カリ酸化分解による椈リグニンの *p*–ヒドロキシフエニル核の検索
藤井俊太郎[*1]、京極与寿郎[*2]、八浜義和[*2]
[*1] 興国人絹パルプ株式会社、[*2] 大阪大学工学部

Search of *p*-hydroxyphenyl nucleus in beech lignin by potassium permanganate oxidation
*1Shuntaro Fujii, *2Yojyuro Kyogoku, *2Yoshikazu Hachihama
*1Koukoku Jinken Pulp Co. Ltd, *2Faculty of Engineering, Osaka University
Keywords: *p*-hydroxyphenyl nucleus, paper chromatography, condensed structure

1960-019
硫化物により生成するアセトバニロン構造の起源
右田伸彦、石津　教
東京大学農学部
Origin of acetovanillone structure formed by sodium hydrosulfide cooking of wood
Nobuhiko Migita, Atsusi Ishizu
Faculty of Agriculture, the University of Tokyo
Keywords: retro-aldol reaction, lignin model compounds

1960-020
リグニン加水分解物としてのコニフェリルアルコールの生成
榊原　彰、中山信子
林業試験場
Formation of coniferyl alcohol as a hydrolysis product of lignin
Akira Sakakibara, Nobuko Nakayama
Forestry and Forest Product Research Institute
Keywords: Yezo spruce, *Picea jezoensis*, coniferyl aldehyde, dehydrodiconiferyl alcohol

1960-021
アルカリ分解物としてのシリンギルエタン
田中治郎
林業試験場
Syringylethane as an alkaline degradation product of lignin.
Jiro Tanaka
Forestry and Forest Product Research Institute
Keywords: beech, *Fagus crenata*, syringylethane

第 6 回 (1961.11.18-19) 大阪、府立農林会館

1961-001
Björkman リグニンについて
John S. Fujii. 中野準三、Bengt Rånby
ニューヨーク州立大学
Studies on the Björkman lignin
John S. Fujii, Junzo Nakano, Bengt Rånby
New York State University
Keywords: polystyrene, change of molecular weight, free-radical, toluene

1961-002
リグニンのポーラログラフイー
寺島典二、神田 孝
名古屋大学農学部
Polarography of lignin
Noritsugu Terashima, Takashi Kanda
Faculty of Agriculture, Nagoya University
Keywords: thiolignin, imine cobalt chelate compound,

1961-003
幼植物のリグニンについて（第 3 報）ニセアカシアの MWL の赤外および紫外線吸収曲線について
川村一次、樋口隆昌
岐阜大学農学部
On the juvenile plant lignin (III), Infrared and ultraviolet absorption spectra of MWL from locust tree
Ichiji Kawamura, Takayoshi Higuchi
Faculty of Agriculture, Gifu University
Keywords: Mayapis, *Shorea palosapis*, Ginkgo, *Ginkgo biloba*

1961-004
リグニンの単離および単離リグニンの反応性
福渡七郎、久下 喬
島根農科大学
Isolation and reactivity of lignin
Shichiro Fukuwatari, Takashi Kuge
Shimane University of Agriculture
Keywords: soda lignin, thiolignin, sulfuric acid lignin

1961-005
クラフト蒸煮における硫化物の役割
石津 敦、右田伸彦
東京大学農学部
Role of sulfide in kraft cooking
Atsushi Ishizu, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: lignin model compound, veratrylglycerol-β-guaiacyl ether, α-(2-methoxyphenoxy)-β-hydroxypropioveratrone, pH, sulfidity

1961-006
亜硫酸パルプ廃液よりリグニンを採取する方法について
久保輝雄、鹿島 寛
野口研究所
Separation of lignin from sulfite pulping black liquor
Teruo Kubo, Hiroshi Kashima

Noguchi Institute
Keywords: lignosulfonate, concentrated black liquor

1961-007
リグニン水素添加分解生成物の分析 — モノフェノール類について
渡辺 浩、鹿島 寛
野口研究所
Analysis of lignin hydrogenolysis products, – Monophenols
Hiroshi Watanabe, Hiroshi Kashima
Noguchi Institute
Keywords: phenol, *o*-cresol, *p*-cresol, *p*-ethylphenol, 2,4-xylenol, *p*-n-propylphenol

1961-008
リグニンの水素添加分解について
尾上史郎, 大久保正道, 岡部次郎
山陽パルプ株式会社
Hydrocracking of lignin
Shiro Onoe, Masamichi Okubo, Jiro Okabe
Sanyo Pulp Co., Ltd.
Keywords: wood meal, hydrochloric acid lignin, sulfuric acid lignin, lignosulfonic acid, Raney-nickel

1961-009
リグニンの水素添加分解に関する研究
榊原 彰[*1]、阿部 勲[*2]
[*1] 林業試験場、[*2]北海道林産試験場
Hydrogenolysis of lignin
Akira Sakakibara[*1], Isao Abe[*2]
[*1]Forestry and Forest Products Research Institute, [*2]Hokkaido Forest Products Research Institute
Keywords: catalyst, low-boiling point phenols

1961-010
ジオキサン一水によるリグニンの加水分解（第 2 報）
榊原 彰、中山信子
林業試験場
Hydrolysis of lignin with dioxane and water
Akira Sakakibara, Nobuko Nakayama
Forestry and Forest Product Research Institute
Keywords: Klason lignin, Yezo spruce, *Picea jezoencis*, beech, *Fagus crenata*

1961-011
木材のアセチルブロマイドによる分解
田中治郎、榊原 彰
林業試験場
Degradation of wood by acetyl bromide
Jiro Tanaka, Akira Sakakibara
Forestry and Forest Products Research Institute
Keywords: syringyl ethane, beech, degradation by alkali

1961-012
木材加水分解リグニンの利用について 1. アルカリによる活性化
森 滋[*1]、山岸祥恭[*1]、半沢道郎[*2]、川瀬 清[*2]、笹谷宣志[*2]
[*1] 北海道林産試験場、[*2] 北海道大学農学部
Utilization of wood hydrolysis lignin, I. Activation by alkali treatment
Shigeru Mori[*1], Yoshiyasu Yamagishi[*1], Michio Hanzawa[*2], Kiyoshi Kawase[*2], Takashi Sasaya[*2]

[*1]Hokkaido Forest Products Research Institute, [*2]Faculty of Agriculture, Hokkaido University
Keywords: *Betula platyphylla*, acid hydrolysis lignin, phenol resin

1961-013
木材加水分解リグニンの利用について 2. 硫酸による活性炭の製造
半沢道郎、里中聖一、氏家雅男
北海道大学農学部
Utilization of wood hydrolysis lignin (II), Production of activated charcoal using sulfuric acid
Michio Hanzawa, Seiichi Satonaka, Masao Ujiie
Faculty of Agriculture, Hokkaido University
Keywords: white birch, *Betula platyphylla*, acid hydrolysis lignin, methylene blue

1961-014
中性亜硫酸セミケミカルパルプ廃液中のリグニンの性状並びに定量法の検討
幡 克美、十河村男
香川大学農学部
Properties and quantitative analysis of lignin in waste liquor of neutral sulfite semi-chemical pulping
Katsumi Hata, Murao Sogo
Faculty of Agriculture, Kagawa University
Keywords: tannin, tannin sulfonic acid, lignin sulfonic acid, colloid titration method

1961-015
中性亜硫酸セミケミカルパルプ廃液のイオン交換樹脂膜透析
幡 克美、十河村男
香川大学農学部
Dialysis of waste liquor of neutral sulfite semi-chemical pulping through ion-exchange resin membranes
Katsumi Hata, Murao Sogo
Faculty of Agriculture, Kagawa University
Keywords: lignin sulfonic acid, free inorganic salt

1961-016
リグニンスルホン酸による可溶化（I）
林 晄、舘 勇、小島義一、東辻 健、坂口 享
京都大学農学部
Solubilization by lignosulfonate (I)
Akira Hayashi, Isamu Tachi, Giichi Kojima, Ken Higashitsuji, Toru Sakaguchi
Faculty of Agriculture, Kyoto University
Keywords: electric conductivity, diffusion coefficient, surface tension

1961-017
リグニンスルホン酸による可溶化（II）
林 晄、舘 勇、東辻 健、坂口 享, 小島義一
京都大学農学部
Solubilization by lignosulfonate (II)
Akira Hayashi, Isamu Tachi, Takeshi Azumatsuji, Ken Higashitsuji, Giichi Kojima
Faculty of Agriculture, Kyoto University
Keywords:pinocyanol chloride, micelle formation

1961-018
重クロム酸加里によるリグニンのゲル化機構について
千手諒一、阿部 光
九州大学農学部
Gelation mechanism of lignin by potassium dichromate
Ryoichi Senjyu, Hikaru Abe

Faculty of Agriculture, Kyusyu University
Keywords: electric conductivity, thiolignin, cross linking

1961-019
リグニンスルホン酸の分子形態についての考察
京極与寿郎、八浜義和
大阪大学工学部
Consideration for molecular configuration of lignin sulfonic acid
Yoshiro Kyogoku, Yoshikazu Hachihama
Faculty of Engineering, Osaka University.
Keywords: molecular weight, sedimentation coefficient, viscosity

1961-020
リグニンの物理化学的研究（第 3 報）微分容量と吸着動力学
上田静男、辻　福寿、渡辺　昌
京都大学化学研究所
Physicochemical study of lignin (III), Differential capacity and adsorption dynamics
Shizuo Ueda, Fukujyu Tsuji, Akira Watanabe
Chemisrtry Institute, Kyoto University
Keywords: dropping mercury electrode

1961-021
リグニンの物理化学的研究（第 4 報）リグニンスルホン酸(LSA)イオンの水銀面への吸着エネルギー
上田静男、辻　福寿、渡辺　昌
京都大学化学研究所
Physicochemical study of lignin (IV), Adsorption energy of lignin sulfonic acid ion on mercury surface
Shizuo Ueda, Fukujyu Tsuji, Akira Watanabe
Institute for Chemical Research, Kyoto University
Keywords: surface active agent, electrical double layer

1961-022
単離した塩素化リグニンスルホン酸バリウムについて
佐藤孝一郎、小林晃夫、三川　礼
国策パルプ株式会社
Properties of isolated chlorinated barium lignosulfonate
Koichiro Sato, Akio Kobayashi, Rei Mikawa
Kokusaku Pulp Co., Ltd.
Keywords: acidic groups, carboxylic group, molecular weight，potentiometric titration

特別講演
米国リグニン化学討論会に出席して
鹿島　寛
野口研究所
1961-Invited lecture:
A report on the Lignin Chemistry Symposium in USA.
Hiroshi Kashima
Noguchi Institute

第7回 (1962.10.04-05) 北海道大学クラーク会館

1962-001
リグニンの単離及び単離リグニンの反応性（IV） 特にヂメチルスルフオキサイド・リグニンについて
福渡七郎、久下　喬、神保幹夫
島根農科大学
Isolation of lignin and reactivity of the isolated lignin (IV), On the dimethylsulfoxide-lignin
Shichiro Fukuwatari, Takashi Hisashita, Mikio Jinbo
Shimane University of Agriculture
Keywords: red pine, *Pinus densiflora,* methoxyl content, UV absorption spectrum, hydroxyl group content

1962-002
Mäule 反応の呈色機構（VI）
中野準三、右田伸彦
東京大学農学部
Mechanism of Mäule color reaction (VI)
Junzo Nakano, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo.
Keywords: biosynthetic lignin, DHP, infrared absorption spectrum

1962-003
ヂオキサン―水によるリグニンの加水分解（第 4 報）
榊原　彰、 中山信子
林業試験場
Hydrolysis of lignin by dioxane-water (IV)
Akira Sakakibara, Nobuko Nakayama
Forestry and Forest Products Research Institute
Keywords: guaiacylglycerol

1962-004
液体アンモニヤ中の金属ナトリウムによるリグニンの分解
榊原　彰，山口　彰
林業試験場
Degradation of lignin by metallic sodium in liquid ammonia
Akira Sakakibara, Akira Yamaguchi
Forestry and Forest Products Research Institute
Keywords: *Picea jezoensis*, dihydroeugenol, guaiacylglycerol

1962-005
リグニンの水素化分解に関する研究
榊原　彰[*1]、尾田勝夫[*1]、阿部　勲[*2]
[*1] 林業試験場、[*2] 北海道林産試験場
Hydrogenolysis of lignin
Akira Sakakibara[*1], Masao Oda[*1], Isao Abe[*2]
[*1]Forestry and Forest Products Research Institute, [*2]Hokkaido Forest Produvts Research Institute
Keywords: catalyst, nickel carbonyl, iron carbonyl, catechols

1962-006
リグニンのメルカプトリシスについて
石原達夫、榊原　彰
林業試験場
Mercaptolysis of lignin
Tatsuo Ishihara, Akira Sakakibara
Forestry and Forest Products Research Institute

Keywords: *Picea jezpensis*, mercaptolysis products, structure of products

1962-007
竹リグニンに関するする研究（第 2 報）ニトロベンゼン酸化による*p*-ヒドロキシベンズアルデヒの成因
前田信夫、五十野善四郎、大野一月
大阪府立大学農学部
Studies on the bamboo lignin (II), Origin of *p*-hydroxybenzaldehyde by nitrobenzene oxidation
Nobuo Maeda, Zenshiro Isono, Kazuki Ono
Faculty of Agriculture, Osaka Prefecture University
Keywords: *p*-hydroxyphenyl nucleus, Hibbert's ketones, *p*-coumaric acid

1962-008
リグニンスルホン酸バリウムの分散性
小林晃夫，葉賀忠昭，佐藤孝一郎
国策パルプ株式会社
Dispersing ability of barium lignosulfonate
Akio Kobayashi, Tadaaki Haga, Koichiro Sato
Kokusaku Pulp Co., Ltd.
Keywords: molecular weight, sulfonic group

1962-009
リグニンスルホン酸のポーラログラフによる定量
林　晄、山条弘子[*1]、小島義一[*2]
[*1] 立命館大学理工学部、[*2] 丸菱油脂株式会社
Quantitative determination of lignin sulfonic acid by polarography
Akira Hayashi[*1], Hiroko Yamajyo[*1], Gi-ichi Kojima[*2]
[*1]College of Science and Engineering, Ritsumeikan University, [*2]Marubishi Oil Chemical Co. Ltd
Keywords: methylene blue, catalytic wave

1962-010
リグニンスルホン酸のキレート作用（1）
林　晄、山条弘子、羽下利勝
立命館大学理工学部
Chelating property of lignosulfonic acid (I)
Akira Hayashi, Hiroko Yamajyou, Toshikatsu Hage
College of Science and Engineering, Ritsumeikan University
Keywords: polarography, ferric ion, catalytic wave

1962-011
リグニンスルホン酸のキレート作用（2）
林　晄、山条弘子、扇孝三郎
立命館大学理工学部
Chelating property of lignosulfonic acid (II)
Akira Hayashi, Hiroko Yamajyou, Kozaburo Ougi
College of Science and Engineering, Ritsumeikan University
Keywords: polarography, ferric ion, catalytic wave, titration curve, ionic linkage

1962-012
リグニンスルホン酸と塩素との反応
尾上史郎，大久保正道，中島浩二
山陽パルプ株式会社
Reaction of lignosulfonic acid with chlorine
Shiro Onoe, Masamichi Okubo, Koji Nakajima
Sanyo Pulp Co., Ltd.

Keywords: sulfite pulp, spent liquor, lignosulfonic acid, chlorination, oxidation, substitution

1962-013
イオン交換繊維によるリグニンスルホン酸の吸着
平山謙三郎，日向明，加藤正明
東洋紡績株式会社
Adsorption of lignosulfonetes with ion-exchange cellulose fiber
Kenzaburo Hirayama, Akira Hyuga, Masaaki Kato
Toyobo Co., Ltd.
Keywords: sulfite spent siquor, lignosulfonates, anion-exchange resin, ion-exchange cellulose, aminoethyl cellulose

1962-014
腐朽材のリグニン
川瀬　清
北海道大学農学部
Lignin in rotten wood
Kiyoshi Kawase
Faculty of Agriculture, Hokkaido University
Keywords: UV spectrometric analysis

1962-015
モクマオウ及びバッカリス材のリグニンについて
川村一次、樋口隆昌
岐阜大学農学部
Studies on the lignin in *Casuarina equisetifolia* and *Baccharis halimifolia*
Takamasa Higuchi, Ichiji Kawamura
Faculty of Agriculture, Gifu University
Keywords: Mäure color reaction, Cross Bevan color reaction, IR absorption specrum, dioxane lignin

1962-016
セミケミカルパルプ廃夜中のリグニンの性状　–とくにメトキシル基について
幡　克美、十河村男
香川大学農学部
Properties of lignin in waste liquor of semi-chemical pulping, especially on the methoxyl content
Katsumi Hata, Murao Sogo
Faculty of Agriculture, Kagawa University
Keywords: chestnut, beech, nitrobenzene oxidation, syringaldehyde, vanillin

1962-017
N–L材混合チオリグニンのIR吸収
杉松昭人，岩田秀子
国策パルプ株式会社
Infrared spectroscopy of a mixture of softwood and hardwood thiolignins
Akihito Sugimatsu, Hideko Iwata
Kokusaku Pulp Co., Ltd.
Keywords: thiolignin, softwood, hardwood, mixture ratio, infrared spectroscopy

1962-018
チオリグニンの過安息香酸分解について
鍵野豊祐、中野準三、右田伸彦
東京大学農学部
Degradation of thiolignin by perbenzoic acid
Toyosuke Kagino, Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo
Keywords: acetovanillone, acetoveratrone, propiovanillone, propioveratrone

1962-019
アルカリリグニン中のカルボニル溝造
石津　敦、仙頭　明、右田伸彦
東京大学農学部
Carbonyl structure in alkali lignin
Atsushi Ishizu, Akira Sento, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: spruce, thiolignin, soda lignin, □□r spectrum

1962-020
サルフエート蒸解における硫化物の役割
石津　敦、中野準三、右田伸彦
東京大学農学部
Role of sulfides in sulfate cooking
Atsushi Ishizu, Junzo Nakano, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: lignin model compounds, guaiacylglycerol-β-guaiacyl ether

1962-021
木材加水分解リグニンの水溶性処理
中野準三、佐々木和仁、右田伸彦
東京大学農学部
Solubilization of wood hydrolysis lignin
Junzo Nakano, Kazuhito Sasaki, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: sufonation, sodium sulfite

1962-022
濃硫酸法木材加水分解リグニンの物理化学的性状について（その一）
布村昭夫、阿部　勲、長谷川勇、峰村伸哉、北村維朗
北海道林業試験場
Physicochemical properties of wood hydrolysis lignin with concentrated sulfuric acid (I)
Akio Nunomura, Isao Abe, Isamu Hasegawa, Nobuya Minemura, Tadao Kitamura
Hokkaido Forestry Research Institute
Keywords: white birch, *Betula platypylla*, methoxyl content

1962-023
リグニン樹脂に関する研究
岡田稔，後藤孝，白岩治巳，高安信義
興国人絹パルプ株式会社
Studies on lignin resin
Minoru Okada, Takashi Goto, Harumi Shiroiwa, Nobuyoshi Takayasu
Kokoku Jinken Pulp Co., Ltd.
Keywords: sulfite lignin, sulfite spent Liquor, polyamine lignin complex, lignin-phenol- formaldehyde resin

1962-024
リグニンスルホン酸−フェノール縮合物の鞣皮性能
京極与寿郎、加藤正之、八浜義和
大阪大学工学部
Tanning property of condensation product of lignosulfonic acid and phenol

Yoshiro Kyougoku, Masayuki Kato, Yoshikazu Hachihama
Faculty of Engineering, Osaka University
Keywords: red pine, *Pinus densiflora,* waste lignin from neutral sulfite cooking, phenolic hydroxyl content

特別誇演、
木材加水分解工業の二、三の知見
保坂秀明
北海道木材化学株式会社
1962-Invited lecture:
Information concerning wood hydrolysis industry
Hideaki Hosaka
Hokkaido Wood Chemical Co. Ltd.

第8回（1963.11.5-6）松江市、島根自治会館

1963-001
ペルオキシダーゼによるコニフェリルアルコールの脱水素重合 1. タケノコのペルオキシダー ゼの精製と脱水素重合物の分光学的検索法
野津祐三、 中村 亘、奥貫一男
大阪大学理学部
Dehydrogenative polymerization of coniferyl alcohol by peroxidase (I), Purification of bamboo peroxidase and spectroscopic investigation of dehydrogenative polymer
Yuzo Nozu, Wataru Nakamura, Kazuo Okunuki
Faculty of Science, Osaka University
Keywords: DHP, UV spectroscopy, optimum pH

1963-002
パーオキシダーゼによるリグニン及びモデル化合物の酵素的分解
石川久雄、沖 妙
愛媛大学農学部
Enzymatic degradation of lignin and lignin model compounds by peroxidase
Hisao Ishikawa, Tae Oki
Faculty of Agriculture, Ehime University
Keywords: radish, horse radish, *Collybia velutipes*

1963-003
アカマツ外皮リグニンスルフォン酸の性状について
十河村男、幡 克美
香川大学農学部
Properties of lignosulfonic acid from outer bark of red pine
Murao Sogo, Katsumi Hata
Faculty of Agriculture, Kagawa University
Keywords: nitrobenzene oxidation, molecular weight

1963-004
ポリサルフアイドリグニンの性状
中野準三、右田伸彦
東京大学農学部
Properties of lignin from polysulfide cooking liquor
Junzo Nakano, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: lignin model compound, vanillyl alcohol, apocynol

1963-005
タバコリグニンの性状について
加藤邦雄[*1]、中野準三[*2]、右田伸彦[*2]
[*1]専売公社中央研究所、[*2]東京大学農学部
Properties of lignin in tobacco plant
Kunio Kato[*1], Junzo Nakano[*2], Nobuhiko Migita[*3]
[*1]Central Research Institute, Japan Tobacco and Salt Public Corporation,
[*2]Faculty of Agriculture, the University of Tokyo
Keywords: milled wood lignin, elemental composition, UV absorption spectrum, IR absorption spectrum

1963-006
ササのリグニンの性質
氏家雅男
北海道大学農学部

Properties of lignin in *Sasa kurilensis*
Masao Uji-ie
Faculty of Agriculture, Hokkaido University
Keywords: *Sasa kurilensis*, milled wood lignin, color reaction, UV absorption spectrum, IR absorption spectrum

1963-007
木材の MWL の赤外線吸収曲線について
川村一次、樋口隆昌
岐阜大学農学部
Infrared absorption spectra of milled wood lignins
Ichiji Kawamura, Takamasa Higuchi
Faculty of Agriculture, Gifu University
Keywords: softwood, hardwood, monocotyledons, dioxane lignin

1963-008
アルカリリグニンのカルボキシル基
石津　敦、中野準三、右田伸彦
東京大学農学部
Carboxyl group in alkali lignin
Atsushi Ishizu, Junzo Nakano, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: protolignin, decarboxylation, Mannich reaction

特別講演
リグニンの工業的利用
野村順次
山陽パルプ株式会社
1963- Invited lecture:
Industrial utilization of lignin
Junji Nomura
Sanyo Pulp Co. Ltd.

パネル討論会、リグニンの利用開発
司会者：八浜義和（大阪大学工学部）
1963- Panel discussion: Development of lignin utilization
Moderator: Yoshikazu Hachihama, Faculty of Engineering, Osaka University

1963-009
リグニンのゲル化、特にその活性中心について
田中浩雄、千手諒一
九州大学農学部
Gelation of lignin, especially on the active center for gel formation
Hirowo Tanaka, Ryouichi Senjyu
Faculty of Agriculture, Kyushu University
Keywords: lignosulfonic acid, thiolignin, potassium dichromate, desulfonation, carboxymethylation, methylation, chlorination

1963-010
リグニンスルフォン酸塩の分散性
小林晃夫、山川　功、葉賀忠昭、佐藤孝一郎
国策パルプ株式会社
Dispersing ability of lignosulfonate
Akio Kobayashi, Isao Yamakawa, Tada-aki Haga, Kouichiro Sato

Kokusaku Pulp Co., Ltd.
Keywords: cement, molecular weight,

1963-011
リグニンに対する放射線グラフト共重合
越島哲夫、村木永之介
大阪工業技術試験所
Radiation–induced graft copolymerization onto lignin
Tetsuo Koshijima, Einosuke Muraki
Osaka National Research Institute.
Keywords: methyl metacrylate, styrene, vinyl acetate, cobalt 60

1963-012
糖化リグニンの溶解とIRスペクトル （リグニンの単離及び単離リグニンの反応性、V）
福渡七郎、雑賀宏昌
島根農科大学
Isolation of lignin and reactivity of the isolated lignin (V), Solubilization of wood-hydolysis lignin, and its infrared absorption spectroscopy
Shichiro Fukuwatari, Hiromasa Saika
Shimane University of Agriculture
Keywords: sulfuric acid lignin, IR spectroscopy

1963-013
ポリサルフアイド2段蒸解におけるリグニンの挙動
宮尾再青[*1]、中野準三[*2]、右田伸彦[*2]
[*1]東洋パルプ株式会社、[*2]東京大学農学部
Behavior of lignin during two-stage polysulfide cooking
Saisei Miyao[*1], Junzo Nakano[*2], Nobuhiko Migita[*2]
[*1]Toyo Pulp Co. Ltd., [*2]Faculty of Agriculture, the University of Tokyo
Keywords: Polysulfide, two-stage cooking, vanillyl alcohol.

1963-014
特別講演、
リグニン化学の一動向
石川久雄
愛媛大学農学部
Invited lecture:
Trend of lignin chemistry
Hisao Ishikawa
Faculty of Agriculture, Ehime University

1963-015
土壌処理剤としてのリグニンスルフォン酸塩の研究 2. ゲル化による砂質土の処理
赤羽政亮、黒沢 彰、矢野弘子
鉄道技術研究所
Studies on lignosulfonate as a soil-stabilizer (II), Treatment of sandy soil by gelation
Masasuke Akabane, Akira Kurosawa, Hiroko Yano
Railway Technical Research Institute
Keywords: potassium dichromate, aluminum chloride, cupric chloride, ferric chloride, aging test

1963-016
土壌処理剤としてのリグニンスルフォン酸塩の研究 3. クロムリグニン及び処理土からの溶脱
赤羽政亮、黒沢 彰、矢野弘子
鉄道技術研究所

Studies on lignosulfonate as a soil-stabilizer (III), Chrom-lignin and its leaching from treated soil
Masasuke Akabane, Akira Kurosawa, Hiroko Yano
Railway Technical Research Institute
Keywords: potassium dichromate, aluminum chloride, cupric chloride, ferric chloride, aging test

1963-017
クラフトリグニンの水素添加分解について
藤岡靖雄
日本パルプ工業株式会社
Hydrocrackinng of kraft lignin
Yasuo Fujioka
Nippon Pulp Industry Co., Ltd.
Keywords: hydrocracking, kraft lignin, oil yield, catalyst, phenols

1963-018
連続試験装置によるリグニンの水素化分解（予報）
榊原 彰、宮崎 信、石原達夫、尾田勝夫、山口 章、高橋 敏
林業試験場
Continuous hydrocracking of lignin by small-scale pilot plant (Preliminary report)
Akira Sakakibara, Sin Miyazaki, Tatsuo Ishihara, Masao Oda, Akira Yamaguchi, Satoshi Takahashi
Forestry and Forest Product Research Institute

特別講演
1963- Invited Lecture:
The Swedish Wood Research Center, a Brief Review of Organization and Research
J. L. Samuelsson
The Central Laboratory of the Swedish Cellulose Industry

第 9 回 (1964.11.11-12) 紙パルプ会館

1964-001
コニフェリルアルコールの脱水素重合に関する酵素系について
中村 亘、野津祐三、奥貫一男
大阪大学理学部
Enzymes participating in dehydrogenative polymerization of coniferyl alcohol
Wataru Nakamura, Yuzo Nozu, Kazuo Okunuki
Faculty of Science, Osaka University
Keywords: peroxidase, laccase, Japanese lacquer, bamboo shoot, mushroom

1964-002
植物の組織培養中のリグニンの生合成
樋口隆昌
岐阜大学農学部
Biosynthesis of lignin during tissue culturing of plants
Takayoshi Higuchi
Facuty of Agriculture, Gifu University
Keywords: strobus pine (*Pinus strobus*), sequoia (*Sequoia sempervirens*), paulownia (*Paulownia tomentosa*), syringe (*Syringa pekinensis*), rosa (*Rosa grauca*), pelargonium (*Pelargonium grandiflorum*), poplar (*Populus nigra*), ^{14}C-phenylalanine, ethanolysis, nitrobenzene oxidation

1964-003
赤外線吸収曲線に基づくリグニンの分別と化学的性質との関係
川村一次、樋口隆昌
岐阜大学農学部
Relationship between classification of lignin based on IR absorption spectra and their chemical properties

Ichiji Kawamura, Takayoshi Higuchi
Facuty of Agriculture, Gifu University
Keywords: fern plant (Pteridophyta), cycads (*Cycas revoluta*), ginkgo (*Ginkgo biloba*), ephedra (*Ephedra sinica*), Mäule color reaction, nitrobenzene oxidation

1964-004
リグニンのポーラログラフ的研究（第 11 報）モデル化合物の KP 蒸解とポーラログラフ的性質
寺島典二、玉生征人、神田 孝
名古屋大学農学部
Polarography of lignin, XI. Kaft cooking of lignin model compounds and their polarographic properties
Noritsugu Terashima, Masato Tamao, Takashi Kanda
Faculty of Agriculture, Nagoya University
Keywords: imine-cobalt chelate compound

1964-005
リグニン中のピノレジノール構造について
荻山紘一、近藤民雄
九州大学農学部
Pinoresinol structural units in lignin molecule
Koichi Ogiyama, Tamio Kondo
Faculty of Agriculture, Kyusyu University
Keywords: red pine, *Pinus densiflora*, *Cryptomeria japonica*, white birch, *Betula tauschii*, *Symplocos lucida*, alcohol lignin, nitric acid oxidation, dilactone

1964-006
低分子量リグニンスルホン酸の分離（主としてペーパークロマトグラフイによる知見）

田中治郎
林業試験場
Separation of low molecular lignosulfonic acid, and information obtained by paper chromatography
Jiro Tanaka
Forestry and Forest Product Research Institute
Keywords: *Abies sachariensis*, sulfite cooking, paper chromatography

1964-007
ブナリグニンスルホン酸に関する研究（第 1 報）
秦　邦男、中村孝一
東北パルプ株式会社
Studies on beech lignosulfonates (I)
Kunio Hata, Koichi Nakamura
Tohoku Pulp Co., Ltd.
Keywords: sulfite spent liquor, barium lignosulfonate, beech, *Fagus crenata*

1964-008
クラフト蒸解における硫化物の役割
石津　敦、中野準三、右田伸彦
東京大学農学部
Role of sulfides in kraft cooking
Atsushi Ishizu, Junzo Nakano, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: *Abies sachariensis*, milled wood lignin, □□r spectrum

1964-009
ポリスルフイドリグニンの性状
*1中野準三、*1右田伸彦、*2宮尾再青
*1東京大学農学部、*2東洋パルプ株式会社
Characterization of lignin from polysulfide cooking liquor
Junzo Nakano, Nobuhiko Migita, Saisei Miyao
*1Faculty of Agriculture, the University of Tokyo, *2Toyo Pulp Co, Ltd.
Keywords: vanillyl alcohol, thiolignin, sulfur content

1964-010
チオリグニンとフェノールとの反応
小林晃夫、葉賀忠昭、佐藤孝一郎
国策パルプ株式会社
Reaction of thiolignin with phenol
Akio Kobayashi, Tadaaki Haga, Kouichiro Sato
Kokusaku Pulp Co., Ltd.
Keywords: thiolignin, phenol, reaction, formaldehyde

1964-011
リグニンをベースとした接着剤について
秋野精也、岩崎揮一、三輪一迪
東海パルプ株式会社
Lignin-base adhesive
Seiya Akino, Terukazu Iwasaki, Kazumichi Miwa
Tokai Pulp & Paper Co., Ltd.
Keywords: thiolignin, phenol-formaldehyde resin, resol resin, softwood black liquor

1964-012
セメントに対する亜硫酸パルプ排液の作用

町原　晃、中島浩二
山陽パルプ株式会社
Dispersing ability of sulfite spent liquor on cement slurry
Akira Machihara, Koji Nakajima
Sanyo Pulp Co., Ltd.

Keywords: sulfite pulp, spent liquor, cement, dispersing effect, lignosulfonic acid, sulfonated carbohydrate, aldonic acid

1964-013
エゾマツ粗酢酸リグニンより得た低分子化合物および高分子化合物について
福住俊郎、芝本武夫
東京大学農学部
Low and high molecular weight compounds obtained from crude acetic acid lignin of Yezo spruce
Toshio Fukuzumi, Takeo Shibamoto
Faculty of Agriculture, the University of Tokyo
Keywords: *Picea jezoensis*, vanilloyl methyl ketone, vanillin, molecular weight

1964-014
リグニンの過酢酸分解について
畠山兵衛、中野準三、右田伸彦
東京大学農学部
Degradation of lignin with peracetic acid
Hyoe Hatakeyama, Jyunzo Nakano, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: lignin model compounds, vanillyl alcohol, veratryl alcohol

1964-015
リグニンの酸化分解に関する研究（III）　過酸化物による高収率パルプの漂白時における脱リグニンの機作について
石川久雄、沖　妙
愛媛大学農学部
Studies on the oxidative degradation of lignin (III), Delignification mechanism of peroxide bleaching of high yield pulp
Hisao Ishikawa, Tae Oki
Faculty of Agriculture, Ehime University
Keywords: chemigroundwood pulp, dioxane lignin, peracetic acid

1964-016
硫酸糖化リグニンの化学「シェルモールド用材料としての基礎的知見」
宮崎安太郎[*1]、勝田千昭[*1]、森松久徳[*2]、上ケ島慶一[*2]
[*1]東京教育大学農学部、[*2]北海道木材化学工業株式会社
Chemistry of sulfuric acid hyrolysis lignin: Basic knowledge on the material for shell mold process
Yasutaro Miyazaki[*1], Chiaki Katuta[*1], Hisanori Morimatsu[*2], Keiichi Jyogasima[*2]
[*1]Faculty of Agriculture, Tokyo University of Education, [*2]Hokkaido Wood Chemical Engineering Co. Ltd.

1964-0017
リグニンの水素化分解に関する研究（第 6 報）鉄カーボニルを触媒とした場合のリグニンスル　ホン酸に対する各要因の検討
榊原　彰[*1]、田中治郎[*2]、古屋信子[*2]、宮崎　信[*2]、石原達夫[*2]、尾田勝夫[*2]、山口　彰[*2]、高橋　敏[*2]、志水一允[*2]
[*1]北海道大学農学部、[*2]林業試験場
Hydrogenolysis of lignin (VI), Investigation of factors affecting on reaction during hydrogenolysis of lignosulfonic acid using iron carbonyl as a catalyst
Akira Sakakibara[*1], Jiro Tanaka[*2], Nobuko Furuya[*2], Shin Miyazaki[*2], Tatsuo Ishihara[*2], Masao Oda[*2], Akira

Yamaguchi[*2], Satoshi Takahashi[*2], Kazumasa Simizu[*2]
[*1]Faculty of Agriculture, Hokkaido University, [*2]Forestry and Forest Products Research Institute
Keywords: addition of sulfur, yield of phenolic cpmpounds

1964-018
リグニンの水素化分解に関する研究（第 7 報）モデル化合物の水素化分解によって得られた 2、3 の知見
石原達夫、宮崎 信、田中治郎、尾田勝夫、山口 彰、古屋信子、高橋 敏、志水一允
林業試験場
Hydrocracking of lignin (VII), Information obtained by hydrocracking of lignin model compounds
Tatsuo Ishihara, Sin Miyazaki, Jiro Tanaka, Masao Oda, Akira Yamaguchi, Nobuko Furuya, Satoshi Takahashi, Kazumasa Simizu
Forestry and Forest Products Research Institute
Keywords: lignin model compounds, structure of side chain

1964-019
重クロム酸リグニンのゲル化機構について（その一）
林 晄[*1]、D.A.I.Goring[*2]
[*1]立命館大学理工学部、[*2]カナダ紙パルプ研究所
Gelling mechanism of lignin by dichromate (I)
Akira Hayashi[*1], D.A.I. Goring[*2]
[*1]College of Science and Engineering, Ritsumeikan University, [*2]Pulp and Paper Research Institute of Canada
Keywords: viscosity, hydrophilicity, sulfonic acid group content, catechol group

1964-020
重クロム酸リグニンのゲル化機構について（その二）
林 晄[*1]、D. A. I. Goring[*2]
[*1]立命館大学理工学部、[*2]カナダ紙パルプ研究所
Gelation mechanism of lignin by dichromate (II)
Akira Hayashi[*1], D.A.I. Goring[*2]
[*1]College of Science and Engineering, Ritsumeikan University, [*2]Pulp and Paper Research Institute of Canada
Keywords: active group, tannin, molybdate, tungstate

1964-021
過硫酸塩によるリグニンのゲル化について
田中浩雄、千手諒一
九州大学農学部
Gelation of lignin by persulfate
Hiroo Tanaka, Ryoichi Senjyu
Faculty of Agriculture, Kyusyu University
Keywords: ammonium persulfate, lignin sulfonic acid, thiolignin

1964-022
土壌処理剤としてのリグニンスルホン酸塩の研究、第５報、カビ性試験について
赤羽政亮，河村肇，八木舜治
鉄道技術研究所
Studies on lignosulfonates for soil stabilizer (V), Result of fungus resistance test
Masasuke Akabane, Hajime Kawamura, Shunji Yagi
Railway Technical Research Institute
Keywords: soil stabilizer, chromium lignin, fungus, lignin sulfonate, gelatinizer

1964-023
特別講演：リグニンの研究に対する要望
1. 大学から民間研究機関へ
三川 礼

大阪大学産業科学研究所
2. 民間から国公立研究機関へ
秦　邦男
東北パルプ株式会社
Invited lecture: Requests to the research on lignin
1. From university to private research institutes.
Rei Mikawa,
Institute of Scientific and Industrial Research, Osaka University
2. From private research institutes to university.
Kunio Hata
Tohoku Pulp Co. Ltd.

第10回（1965.11.8-9）大阪科学技術センター

1965-001
加水分解リグニン系樹脂製造に関する研究（第2報）リグニンのアルカリ活性化試験
阿部　勲、窪田　実、布村昭夫、森　滋
北海道林産試験場
Preparation of plastics from wood hydrolysis lignin (II), Activation of lignin by treatment with alkali
Isao Abe, Minoru Kubota, Akio Nunomura, Shigeru Mori
Hokkaido Forest Products Research Institute
Keywords: thermosetting plastic, sulfuric acid lignin

1965-002
加水分解リグニン系樹脂製造に関する研究（第3報）活性化リグニンの縮合試験
阿部　勲、北村維朗、布村昭夫、森　滋
北海道林産試験場
Preparation of plastics from wood hydrolysis lignin (III) Condensation of activated lignin
Isao Abe, Minoru Kubota, Akio Nunomura, Shigeru Mori
Hokkaido Forest Products Research Institute
Keywords: thermosetting plastic, sulfuric acid lignin, phenol, formaldehyde

1965-003
リグニン樹脂のシェルモールドへの応用
広瀬正尚
日本合成化工株式会社
Application of lignin resin for shell mold
Masanao Hirose
Nihon Gosei Kako Co., Ltd.
Keywords: lignin resin, shell mold, phenylpropane radical

1965-004
チオリグニンおよびフェノール化チオリグニンとホルムアルデヒドの反応
小林晃夫，葉賀忠昭，佐藤孝一郎
国策パルプ株式会社
Reaction of thiolignin and phenolated thiolignin with formaldehyde
Akio Kobayashi, Tadaaki Haga, Kouichiro Sato
Kokusaku Pulp Co., Ltd.
Keywords: thiolignin, phenolated thiolignin, formaldehyde, reaction

1965-005
アルカリ電池中のリグニンの挙動
林　晄、名村好文、山下大二郎
立命館大学理工学部
Behavior of lignin in alkaline battery
Akira Hayashi, Yosifumi Namura, Daijiro Yamashita
College of Science and Engineering, Ritsumeikan University
Keywords: thiolignin, electrode reaction

1965-006
亜硫酸パルプ排液の粘結性について
町原　晃，岡部次郎
山陽パルプ株式会社
Adhering ability of sulfite spent liquor
Akira Machihara, Jiro Okabe
Sanyo Pulp Co., Ltd.

Keywords: sulfite pulp, spent liquor, adhering ability, casting sand, lignosulfonic acid, xylose

1965-007
亜硫酸パルプ廃液の 2、3 の粉体に対する分散効果について
猪狩俶将、小川博嗣、生源寺延
東京工業試験所
Dispersion ability of sulfite waste liquor to some kinds of powder material
Yoshimasa Ikari, Hirotsugu Ogawa, Susumu Shogenji
Government Chemical Industrial Research Institute, Tokyo
Keywords: calcium carbonate, calcium hydroxide, Portland cement

1965-008
亜硫酸パルプ廃液およびリグニンスルホン酸の界面活性
小山 実、生源寺延
東京工業試験所
Surface activity of sulfite waste liquor and lignin sulfonic acid
Minoru Koyama, Susumu Shogenji
Government Chemical Industrial Research Institute, Tokyo
Keywords: surface tension, interfacial surface tension, solubilization capacity, emulsifying capacity, dispersion force, osmotic force, foaming power

1965-009
加水分解リグニンから製造した陰イオン交換樹脂
載 清華、中野準三、右田伸彦
東京大学農学部
Anion exchange resin prepared from wood hydrolysis lignin
Seika Tai, Junzo Nakano, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: white birch (*Betula platyphylla*), chloromethylated lignin, quaternary ammonium-strong basic ion-exchange resin

1965-010
リグニンの水素化分解に関する研究 (第 8 報) 再生重質油をペースト油に使用するくりかえし運転について
宮崎 信[*1]、石原達夫[*1]、尾田勝夫[*1]、田中治郎[*1]、山口 彰[*1]、高橋 敏[*1]、古屋信子[*1]、志水 一允[*1]、榊原彰[*2]
[*1] 林業試験場、[*2] 北海道大学農学部
Hydrogenolysis of lignin, VIII. Repeated operation using recovered heavy oil as paste oil
Shin Miyazaki[*1], Tatsuo Ishihara[*1], Masao Oda[*1], Jiro Tanaka[*1], Akira Yamaguchi[*2], Satoshi Takahashi[*1], Nobuko Furuya[*1], Kazumasa Simizu[*1], Akira Sakakibara[*2]
[*1]Forestry and Forest Products Research Institute, [*2]Faculty of Agriculture, Hokkaido University
Keywords: SP waste lignin

1965-011
リグニンの水素化分解に関する研究（第 9 報）リグニンペーストの粘度
山口 彰[*1] 宮崎 信[*1]、石原達夫[*1]、尾田勝夫[*1]、田中治郎[*1]、、高橋 敏[*1]、古屋信子[*1]、志水一允[*1]、榊原彰[*2]
[*1] 林業試験場、[*2] 北海道大学農学部
Hydrogenolysis of lignin (IX), Viscosity of lignin paste
Akira Yamaguchi[*2], Shin Miyazaki[*1], Tatsuo Ishihara[*1], Masao Oda[*1], Jiro Tanaka[*1], Satoshi Takahashi[*1], Nobuko Furuya[*1], Kazumasa Simizu[*1], Akira Sakakibara[*2]
[*1]Forestry and Forest Products Research Institute, [*2]Faculty of Agriculture, Hokkaido University
Keywords: SP waste lignin

1965-012

スチレンのリグニンへの放射線グラフト共重合における溶媒効果
村木永之介、越島哲夫
大阪工業技術試験所
Solvent effect of styrene on radiation-induced graft copolymerization onto lignin
Einosuke Muraki, Tetsuo Koshijima
Government Industrial Research Institute, Osaka
Keywords: red pine (*Pinus densiflora*), hydrochloric acid lignin, methylated lignin, styrene

1965-013
塩酸リグニン・スチレングラフト重合生成物の性状と官能基
越島哲夫、村木永之介
大阪工業技術試験所
Properties and functional groups of hydrochloric acid lignin-styrene graft copolymer
Tetsuo Koshijima, Einosuke Muraki
Government Industrial Research Institute, Osaka
Keywords: nitrobenzene oxidation, chlorite oxidation

1965-014
リグニンモデルのゲル化機構について
田中浩雄、千手諒一
九州大学農学部
Gelation mechanism of lignin model compounds
Hiroo Tanaka, Ryoichi Senjyu
Faculty of Agriculture, Kyusyu University
Keywords: poly-(4-hydroxy)-styrene, novolac type phenolic resin

1965-015
モデル化合物のアルカリ分解生成物より見たリグニン側鎖の構造
田中治郎
林業試験場
Side chain structure of lignin estimated by alkaline degradation of model compounds
Jiro Tanaka
Forestry and Forest Product Research Institute
Keywords: guaiacylethane

1965-016
広葉樹リグニンのアリルグリセロール-β-アリルエーテル型構造について
中野準三、何　照＝、右田伸彦
東京大学農学部
Arylglycerol-β-aryl ether structure in hardwood lignin
Junzo Nakano, Zhao Jun He, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: guaiacyl nucleus, syringyl nucleus, acetoguaiacone, acetosyringone

1965-017
リグニン中のピノレジノール構造について（第 2 報）
荻山紘一、近藤民雄
九州大学農学部
Pinoresinol structural units in lignin molecule (II)
Koichi Ogiyama, Tamio Kondo
Faculty of Agriculture, Kyusyu University
Keywords: ethanol lignin, acetic acid lignin, dioxane lignin, milled wood lignin

1965-018

リグニンの色に関する研究（第 2 報）官能基がチオリグニンの色に及ぼす影響
飯山賢治、中野準三、右田伸彦
東京大学農学部
Studies on the color of lignin (II), Effect of functional groups on the color of thiolignin
Kenji Iiyama, Junzo Nakano, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: methylated lignin, chromophore, auxochrome

1965-019
リグニンの酸・アルカリ変性について
福渡七郎、瀬崎一敏
兵庫農科大学
Modification of lignin by treatment with acid and alkali
Shichiro Fukuwatari, Kazutoshi Sezaki
Hyogo University of Agriculture
Keywords: sulfuric acid lignin, solubility

1965-020
リグニンの酸化分解に関する研究（第 5 報）過酢酸による模型化合物の酸化
石川久雄、沖　妙
愛媛大学農学部
Studies on the oxidative degradation of lignin (V), Oxidation of lignin model compounds by peracetic acid
Hisao Ishikawa, Tae Oki
Faculty of Agriculture, Ehime University
Keywords: guaiacyl methyl carbinol, vanillyl alcohol, acetovanillone, vanillin, vanillic acid

1965-021
リグニンの酸化分解に関する研究（第 6 報）過酸化物漂白によるパルプからの脱リグニンについて
石川久雄、大久保克美、沖　妙
愛媛大学農学部
Studies on the oxidative degradation of lignin (VI), Delignification of pulp by peracetic acid bleaching
Hisao Ishikawa, Katsumi Okubo, Tae Oki
Faculty of Agriculture, Ehime University
Keywords: high yied pulp, semichemical pulp, groundwood pulp, dioxane lignin

1965-022
リグニンの過酢酸分解について（コハク酸の起源構造の追求）
畠山兵衛、中野準三、右田伸彦
東京大学農学部
Degradation of lignin by peracetic acid — Investigation of original structure from which succinic acid is derived

Hyoe Hatakeyama, Junzo Nakano, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: Yezo spruce *(Picea jezoensis)*, succinic acid, vanillyl alcohol, veratryl alcohol

1965-023
リグニンに対する過酢酸の作用（第２報）
坂井克己、近藤民雄
九州大学農学部
Action of peracetic acid on lignin (II)
Kokki Sakai, Tamio Kondo
Faculty of Agriculture, Kyusyu University
Keywords: red pine (*Pinus densiflora*), white birch (*Betula platyphylla*), dioxane lignin, infrared absorption spectrum

1965-024
MWL およびその抽出残渣リグニンの分解物における比較
榊原　彰、松倉紀男
北海道大学農学部
Comparison of degradation products from MWL and residual lignin
Akira Sakakibara, Motoo Matsukura
Faculty of Agriculture, Hokkaido University
Keywords: Yezo spruce (*Picea jezoensis*), veratric acid, isohemipic acid, dehydrodiveratric acid

1965-025
ジオキサン-水によるリグニンの加水分解（第 5 報）モデル物質の分解およびリグニン中における結合形態に対する 2、3 の考察
榊原　彰、武山浩武、諸星紀幸
北海道大学農学部
Hydrolysis of lignin with dioxane and water (V), Hydrolysis of lignin model compounds and discussion of linkage types in lignin
Akira Sakakibara, Hirotake Takeyama, Noriyuki Morohoshi
Faculty of Agriculture, Hokkaido University
Keywords: coniferyl alcohol, veratrylglycerol-β-guaiacyl ether, disproportionation reaction

1965-026
チオ・リグニンの反応、 (その１) スルホ・メチル化反応
品部義秋，小川昭弘
東洋パルプ株式会社
Reaction of thiolignin (I), Sulfomethylation
Yoshiaki Shinabe, Akihiro Ogawa
Toyo Pulp Co., Ltd.
Keywords: dispersing agent, thiolignin, hydrophilicity, sulfomethylation, methylol group, air-entraining ability

1965-027
チオ・リグニンの反応、（その２）アミノ・メチル化反応
品部義秋，小川昭弘
東洋パルプ株式会社
Reaction of thiolignin (II), Aminomethylation
Yoshiaki Shinabe, Akihiro Ogawa
Toyo Pulp Co., Ltd.
Keywords: thiolignin, asphalt emulsifier, cationic surfactant, Mannich reaction

1965-028
チオリグニンのスルホメル化について
老田　靖、中野準三、右田伸彦
東京大学農学部
Sulfomethylation of thiolignin
Yasushi Oita, Junzo Nakano, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: softwood thiolignin, hardwood thiolignin, surface tension, dispersion force

1965-029
竹の維管束および柔細胞のリグニンの化学的性質
木村長治、樋口隆昌、川村一次
岐阜大学農学部
Chemical properties of lignin in vascular bundle and parenchyma of bamboo

Choji Kimura, Takayoshi Higuchi, Ichiji Kawamura
Faculty of Agriculture, Gifu University
Keywords: *Phyllostachys pubescens*, *Phyllostachys reticulata*, nitrobenzene oxidation, ethanolysis

1965-030
種々のリグニン中の *p*-ヒドロキシフェニルグリセロール-β-アリルエーテル構造
樋口隆昌、川村一次
岐阜大学農学部
p-Hydroxyphenylglycerol structures in lignin of various plants
Takayoshi Higuchi, Ichiji Kawamura
Faculty of Agriculture, Gifu University
nitrobenzene oxidation, ethanolysis, gaschromatography, *Gramineae*

1965-031
ペルオキシダーゼによるコニフェリルアルコールの脱水素重合
野津祐三、中村　亘、奥貫一男
大阪大学理学部
Dehydrogenative polymerization of coniferyl alcohol by peroxidase
Yuzo Nozu, Wataru Nakamura, Kazuo Okunuki
Faculty of Science, Osaka University
Keywords: laccase, molecular weight, sinapyl alcohol

1965-総合講演
A　リグニン研究の最近の動向
　中野準三（東京大学農学部）
B　リグニン生合成研究の現状と問題点
　樋口隆昌（岐阜大学農学部）
C　リグニンの利用と物性について
　林　晄（立命館大学）
D　最近のパルプ廃液処理の動向
　野村順次（山陽パルプ株式会社）
1965-Plenary lectures:
A　Recent trends in research of lignin
　Junzo Nakano (Faculty of Agriculture, the University of Tokyo)
B　Current situation of research in lignin biosynthesis and related problems
　Takayoshi Higuchi (Faculty of Agriculture, Gifu University)
C　Physical properties and utilization of lignin
　Akira Hayashi (Ritsumeikan University)
D　Recent trends in pulp waste liquor treatment
　Junji Nomura (Sanyo Pulp Co. Ltd.)

第11回（1966.10.31-11.1）広島大学会館

1966-001
リグニンの色に関する研究（第3報）蒸煮および単離条件がチオリグニンの色に及ぼす影響
飯山賢冶、中野準三、右田伸彦
東京大学農学部
Studies on the color of lignin (III), Effect of cooking and isolation conditions on the color of thiolignin
Kenji Iiyama, Junzo Nakano, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: red pine (*Pinus densiflora*), beech (*Fagus crenata*), reflectance spectra, visible light transmittance, sulfur

1966-002
リグニンの色に関する研究（IV）材のシーズニングがリグノスルホン酸の色に及ぼす影響について
中野準三、飯塚堯介、右田伸彦
東京大学農学部
Studies on the color of lignin (IV), Effect of seasoning on the color of lignosulfonic acid
Junzo Nakano, Gyosuke Meshitsuka, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: *Abies firma, Pinus densiflora, Fagus crenata, Betura Maximowiziana*, brightness, wavelength, excitation purity

1966-003
重金属イオンとリグニンスルホン酸の色
林　晄、三成　紘
立命館大学理工学部
Heavy metai ion and color of lignosulfonic acid
Akira Hayashi, Hiro Mitsunari
College of Science and Engineering, Ritsumeikan University
Keywords: chelation, iron, copper, nickel, cobalt, manganese, chromium, catechol group

1966-004
リグニンのオゾン分解について
畠山兵衛、外岡豊穂、中野準三、右田伸彦
東京大学農学部
Degradation of lignin by ozone
Hyoe Hatakeyama, Toyoho Tonooka, Junzo Nakano, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: vanillyl alcohol, veratryl alcohol, muconic acid lactone

1966-005
リグノスルホン酸およびチオリグニンの過酢酸分解
鈴木金道[＊1]畠山兵衛[＊2]、中野準三[＊2]、右田伸彦[＊2]
[＊1]東北パルプ株式会社研究所、[＊2]東京大学農学部
Degradation of lignosulfonic acid and thiolignin by peracetic acid
Kanemichi Suzuki[*1], Hyoe Hatakeyama[*2], Junzo Nakano[*2], Nobuhiko Migita[*2]
[*1] Institute of Tohoku Pulp Co. Ltd., [*2] Faculty of Agriculture, the University of Tokyo
Keywords: carboxyl group, phenolic hydroxyl group, methoxyl group, UV absorption spectrum

1966-006
二酸化塩素漂白に関する研究（I）モデル物質の二酸化塩素酸化について
石川俊彦、住本昌之、近藤民雄
九州大学農学部
Studies on the bleaching by chlorine dioxide (I), Oxidation of model compounds by chlorine dioxide

Toshihiko Ishikawa, Masayuki Sumimoto, Tamio Kondo
Faculty of Agriculture, Kyusyu University
Keywords: vanillin, vanillyl alcohol, syringyl alcohol, p-quinone structure

1966-007
リグノスルホン酸ゲル化反応中の脱メチル
林　晄、名村好夫、上北忠之
立命館大学理工学部
Demethylation during gelation reaction of lignosulfonic acid
Akira Hayashi, Yoshio Namura, Tadayuki Uekita
College of Science and Engineering, Ritsumeikan University
Keywords: catechol group, dichromate, guaiacol, vanillin, vanillyl alcohol

1966-008
リグニン及びリグニンモデル物質の高分解能 NMR スペクトル
武谷　愿、横山　晋、石井忠雄
北海道大学工学部
High resolution NMR spectroscopy of lignin and lignin model compounds
Gen Taketani, Shin Yokoyama, Tadao Ishii
Faculty of Engineering, Hokkaido University
Keywords: *Abies sachalniensis, Fagus crenata, Quercus crispula*, milled wood lignin, DMSO

1966-009
リグニンと炭水化物との結合について
寺島典二[*1]、H.I. Bolker[*2]
[*1] 名古屋大学農学部、[*2] カナダ紙パルプ研研究所
Linkages between lignin and carbohydrates
Noritsugu Terashima[*1], Henry I. Bolker[*2]
[*1] Faculty of Agriculture, Nagoya University, [*2] Pulp and Paper Research Institute of Canada
Keywords: acetal, 2,2-dimethoxypropane, 2,2-diethoxypropane, solvolysis

1966-010
リグニン中のカルボキシル基定量
福渡七郎、錦織　勇
島根大学農学部
Determination of carboxyl group in lignin
Shichiro Fukuwatari, Isamu Nishikori
Faculty of Agriculture, Shimane University
Keywords: Infrared absorption spectroscopy, potassium thiocyanate, soda-lignin, thiolignin

1966-011
稲科植物 MWL の化学的性質
樋口隆昌[*1]、島田幹夫[*1]、川村一次[*1]、井藤佳美[*2]
[*1]岐阜大学農学部、[*2]岐阜大学工学部
Chemical properties of milled wood lignin from gramineous plants
Takayoshi Higuchi[*1], Mikio Shimada[*1], Ichiji Kawamura[*1], Yoshimi Itoh[*2]
[*1] Faculty of Agriculture, Gifu University,[*2] Faculty of Engineering, Gifu University
Keywords: UV absorption spectroscopy, IR absorption spectroscopy, p-coumaric acid, ferulic acid, ester bond

1966-012
熱帯より温帯にわたり自然分布しているユーカリのリグニンの化学的性質について
川村一次[*1]、D.E. Bland[*2]
[*1]岐阜大学農学部、[*2]オーストラリヤ CSIRO 林産研究所

Chemical properties of lignin of eucalyptus distributed from tropical to temperate zone
Ichiji Kawamura[*1], D.E. Bland[＊2]
[*1] Faculty of Agriculture, Gifu University, [＊2]Forest Product Research Institute, CSIRO, Australia
Keywords: IR absorption spectroscopy, S/V ratio, Klason lignin, altitude effect

1966-013
樹皮リグニンの化学的性質
樋口隆昌[＊1]、島田幹夫[＊1]、川村一次[＊1]、井藤佳美[＊2]
[＊1]岐阜大学農学部、[＊2]岐阜大学工学部
Chemical properties of bark lignin
Takayoshi Higuchi[*1], Mikio Shimada[*1], Ichiji Kawamura[*1], Yoshimi Itoh[*2]
[*1] Faculty of Agriculture, Gifu University,[*2] Faculty of Engineering, Gifu University
Keywords: black pine, *Pinus Thunbergii*, fir, *Abies firma*, hemlock, *Tsuga heterophylla*, Alder, *Alnus japonica*, beech, *Fagus crenata*, ethanolysis

1966-014
ダグラスファー樹皮のエタノリシス生成物
藤井ミチヒロ[*1], E. F. Kurth[*2]
[*1] 北越製紙, [*2] オレゴン州立大
Ethanolysis products from Douglas fir bark
Michihiro Fujii[*1], E. F. Kurth[*2]
[*1]Hokuetsu Paper Mills Co., Ltd., [*2]Oregon State University
Keywords: Douglas fir, *Pseudotsuga taxifolia*, ethanolysis, Hibbert's ketones

1966-015
ブナリグニンスルホン酸に関する研究（第2報）ブナリグニンスルホン酸分劃物のニトロベンゼン酸化
秦邦男, 中村孝一
東北パルプ株式会社
Studies on beech lignosulfonates (II), Nitrobenzene oxidation of fractionated lignosulfunate portions
Kunio Hata, Koichi Nakamura
Tohoku Pulp Co., Ltd.
Keywords: beech lignosulfonates, alkaline nitrobenzene oxidation, vanillin, syringyl aldehyde, *p*-hydroxybenzaldehyde

1966-016
リグニンに対するアルカリ蒸解の影響 (IX) アリルアルキル-β-アリルエーテルの開裂に関するモデル実験
中野準三、鈴木 磨、佐伯節夫、右田伸彦
東京大学農学部
Effect of alkali cooking on lignin (IX), Model experiments on cleavage of arylalkyl-β-aryl ether
Junzo Nakano, Migaku Suzuki, Setsuo Saheki, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: kraft cooking, sulfidity, reaction temperature, paper chromatography, UV absorption spectroscopy

1966-017
ジオキサン一水によるリグニンの加水分解（第 6 報）
佐野嘉拓、榊原 彰
北海道大学農学部
Hydrolysis of lignin with dioxane and water (VI)
Yoshihiro Sano, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: coniferyl alcohol, isoeugenol, paper chromatography

1966-018

プロトリグニンの水素化分解に関する研究（第 1 報）ビフエニール結合体を中心として
和田　功、太田路一、榊原　彰
北海道大学農学部
Hydrogenolysis of protolignin (I), On the biphenyl type products
Isao Wada, Michikazu Ota, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: Yezo spruce, *Picea jezoensis*, paper chromatography, 5,5′-biphenyl compounds

1966-019
モデル化合物のアルカリ分解生成物からみたリグニン側鎖の構造（II）
田中治郎
林業試験場
Side chain structure of lignin estimated from alkaline degradation products of model compounds (II)
Jiro Tanaka
Forestry and Forest Product Research Institute
Keywords: guaiacyl ethane, ferulic acid, acetoguaiacone

1966-020
リグニン中のピノレジノール構造について（第 3 報）2,3-[Bis−oxyvanillyl]-butane-diol(1,4)から *dl*-Pinoresinol の合成について
萩山紘一、近藤民雄
九州大学農学部
Pinoresinol structure in lignin (III), Synthesis of dl-pinoresinol from 2,3-[bis−oxyvanillyl]-butane- diol(1,4)
Koichi Ogiyama, Tamio Kondo
Faculty of Agriculture, Kyusyu University
Keywords: thin layer chromatography, symplocosigenol, epipinoresinol

1966-021
β-ナフタレンスルホン酸ホルムアルデヒド縮合体（リグニンスルホン酸塩類似物質）の薄層クロマトグラフイーによる分離ならびにそれらの分子量と分子構造について
根来健二、佐伯幸民
広島大学工学部
Separation of a condensation product of β-naphthalene sulfonic acid and formaldehyde (a compound analogous to lignin sulfonic acid) by thin layer chromatography, and its molecular weight, and chemical structure
Kenji Negoro, Yukitami Saiki
Faculty of Engineering, Hiroshima University
Keywords: Tamol NNO, Demol N, gel filtration

1966-022
稲科植物リグニンの *P*-ヒドロキシフエニルプロパン部の性質とその形成におけるチラーゼの役割り
樋口隆昌[*1]、川村一次[*1]、井藤佳美[*2]
[*1]岐阜大学農学部、[*2]岐阜大学工学部
Properties of *p*-hydroxyphenylpropane moiety in gramineous plant lignin and role of tyrase in its formation
Takayoshi Higuchi[*1], Ichiji Kawamura[*1], Yosimi Itoh[*2]
[*1] Faculty of Agriculture, Gifu University,[*2] Faculty of Engineering, Gifu University
Keywords: *p*-coumaric acid, *p*-hydroxyphenyl nucleus, phenylalanine-G-^{14}C,tyrosine-G-^{14}C

1966-023
タケノコ中の 5-デヒドロシキミ酸還元酵素
樋口隆昌、島田幹夫
岐阜大学農学部
5-Dehydroshikimic acid reductase in bamboo shoots
Takayoshi Higuchi, Mikio Shimada

Faculty of Agriculture, Gifu University
Keywords: *Phyllostachys reticulata*, shikimic acid pathway, NADP, EDTA

1966-024
酵素によるフエルラ酸およびシナップ酸の生成
樋口隆昌、島田幹夫
岐阜大学農学部
Formation of ferulic and sinapic acids by enzyme
Takayoshi Higuchi, Mikio Shimada
Faculty of Agriculture, Gifu University
Keywords: *Phyllostachys pubescens*, *Phyllostachys reticulata*, S-adenosylmethinine, caffeic acid, 5-dehydroferulic acid

1966-025
キンイロアナタケによって腐朽されたトウヒ材から分離したリグニンについて
幡　克美[*1]、F.F. Nord[*2]
[*1]香川大学農学部、[*2]フオーダム大学
Studies on the lignin isolated from spruce wood rotted by *Poria subacida* B11
Katsumi Hata[*1], F.F. Nord[*2]
[*1]Faculty of Agriculture, Kagawa Universty, [*2]Fordham University
Keywords: spruce, *Picea jezoensis*, milled wood lignin, UV absorption spectrum, IR absorption spectrum, nitrobenzene oxidation

1966-026
リグニンの水素添加分解
大島幹義、鹿島　寛、田畑晴郎、久保輝雄、渡部　浩
野口研究所
亜硫酸パルプ廃液、脱スルホンリグニン、触媒
Hydrocracking of lignin
Mikiyoshi Oshima, Hiroshi Kajima, Haruo Tabata, Teruo Kubo, Hiroshi Watanabe
Noguchi Institute
Keywords: sulfite pulp waste liquor, desulfonated lignin, catalyst

1966-027
鉛蓄電池に対するリグニンの効果
林　晄、名村好文
立命館大学理工学部
Effect of lignin on lead storage battery
Akira Hayashi, Yoshifumi Namura
College of Science and Engineering, Ritsumeikan University
Keywords: alkaline lignin, catechol, maleic acid

1966-028
液相及び気相アルカリ蒸解黒液から単離したリグニンの性状について
岡本行雄[*1]、李　宗藩[*2]、中野準三[*2]、右田伸彦[*2]
[*1]東洋パルプ株式会社、[*2]東京大学農学部
Characteristics of lignins isolated from the black liquor of liquid-phase and vapor-phase alkaline cookings
Yukio Okamoto[*1], Sohan Ri[*2], Junzo Nakano[*2], Nobuhiko Migita[*2]
[*1] Toyo Pulp Co. Ltd., [*2] Faculty of Agriculture, the University of Tokyo
Keywords: alkafide pulping, kraft pulping, polysulfide pulping

1966-029
Na-S 系によるリグニンの脱メチル反応
種田健造、長谷川勇

北海道林産試験場
Demethylation of lignin in aqueous alkaline solution containing sulfur
Kenzo Taneda, Isamu Hasegawa
Hokkaido Forest Products Research Institute
Keywords: dimethyl sifide, acid hydrolysis lignin, conversion to resin

1966-030
亜硫酸パルプ廃液のアルカリ溶液中での挙動について
猪狩俶将、小川博嗣、生源寺延
東京工業試験所
Behavior of lignin in alkaline sulfite black liquor
Yoshimasa Ikari, Hirotsugu Ogawa, Susumu Shogenji
Tokyo Institute of Advanced Industrial Science and Technology
Keywords: calcium hydroxide, cement, conductivity titration

1966-031
粉体の分散に対するリグニンスルホン酸と糖変成物の作用
小川博嗣、猪狩俶将、生源寺延
東京工業試験所
Effect of lignin sulfonic acid and metamorphic product of carbohydrates on dispersion of powder
Hirotsugu Ogawa, Yoshimasa Ikari, Susumu Shogenji
Tokyo Institute of Advanced Industrial Science and Technology
Keywords: zinc powder, light absorption

1966-032
亜硫酸パルプ排液の熱処理による分散剤の製造について
町原　晃，岡部次郎
山陽パルプ株式会社
Preparation of dispersant by heat treatment of sulfite spent liquor
Akira Machihara, Jiro Okabe
Sanyo Pulp Co., Ltd.
Keywords: sulfite pulp, spent liquor, dispersant, heat treatment, spray drying, lignosulfonic acid

1966-033
針葉樹のクラフト黒液からチオリグニンの沈澱
品部義秋、西部隆文
東洋パルプ株式会社
Precipitation of thiolignin from black liquor of kraft cooking of conifer wood
Yoshiaki Shinabe, Takafumi Nishibe
Toyo Pulp Co. Ltd.
Keywords: precipitant, sulfuric acid, carbon dioxide, cohesion property

1966-034
KP 黒液およびチオリグニンの界面活性
小山　実、生源寺延
東京工業試験所
Surface activity of sulfite waste liquor and lignin sulfonic acid
Minoru Koyama, Susumu Shogenji
Tokyo Institute of Advanced Industrial Science and Technology
Keywords: surface tension, solubilization capacity, emulsifying capacity, dispersion force, osmotic force, foaming power

1966-035
チオリグニンの熱的挙動

岩見田　紀，佐藤孝一郎
国策パルプ株式会社
Thermal properties of thiolignin
Tadashi Iwamida, Kouichiro Sato
Kokusaku Pulp Co., Ltd.
Keywords:　thiolignin, thermal gravimetric analysis, differential thermal analysis, insolubility, oxygen content, softening temperature

1966-036
リグニンのエポオキシ化について
戴　洋華、中野準三、右田伸彦
東京大学農学部
Epoxidation of lignin
Seika Tai, Junzo Nakano, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords:　softwood lignin, coniferous wood lignin, epichlorohydrin, infrared spectroscopy

1966-037
フェノール化チオリグニンとヘキサメチレンテトラミンとの反応
小林晃夫，葉賀忠昭，佐藤孝一郎
国策パルプ株式会社
Reaction of phenolated thiolignin with hexamethylene tetramine
Akio Kobayashi, Tadaaki Haga, Kouichiro Sato
Kokusaku Pulp Co., Ltd.
Keywords:　thiolignin, phenolated thiolignin, hexamethylene tetramine, formaldehyde

1966-038
加水分解リグニン系樹脂に関する研究（第 4 報）装置試験および製造原単位
森　滋、布村昭夫、阿部　勲、北村維郎、窪田　実、朝倉孝之、斉藤　勝
北海道林産試験場
Studies on the plastics from wood hydrolysis lignin (IV), Equipment test and production intensity
Shigeru Mori, Akio Nunomura, Isao Abe, Tadao Kitamura, Minoru Kubota, Takayuki Asakura, Masaru Saito
Hokkaido Forest Products Research Institute
Keywords:　thermosetting resin, continuous activation reaction, production intensity, operation cost

1966-特別講演
A
鋳型粘結剤について
東　正十郎
広島県呉工業試験所
1966-Invited lecture: Binder for casting mold
Shojuro Azuma
Kure Institute of Industrial Science and Technology, Hiroshima Prefecture.
Keywords:　bentnite, water glass, sodium silicate, cement, starch, drying oil, lignin binder

B
最近の界面活性剤の物性研究の動向
根来健二
広島大学工学部
1966-Invited lecture: Recent trend in the research of physical property of surfactant
Kenji Negoro
Faculty of Engineering, Hiroshima University
Keywords:　surface tension, surface adsorption, contact angle, cloud point

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1967-001
SP 排液中のリグニンスルホン酸と非リグニン有機物の粉体の分散に対する作用
小川博嗣、猪狩俶将、生源寺延
東京工業試験所
要旨空白（中止）

1967-002
リグニンの過酢酸酸化生成物の性状について
石川久雄、木下良郎、沖　妙、大久保克美
愛媛大学農学部
Characteristics of peracetic acid oxidation product of lignin
Hisao Ishikawa, Yoshiro Kinoshita, Tae Oki, Katumi Okubo
Faculty of Agriculture, Ehime University
Keywords: conifer, dioxane lignin, molecular weight

1967-003
SP 排夜中のリグニンスルホン酸の分子量分布とアルカリ溶液中での挙動
猪狩俶将、小川博嗣、生源寺延
東京工業試験所
Molecular weight distribution of lignin sulfonic acid from sulfite waste liquor and its behavior in alkaline solution
Yoshimasa Ikari, Hirotsugu Ogawa, Susumu Shogenji
Tokyo Institute of Advanced Industrial Science and Technology
Keywords: hyamine salt, quaternary ammonium salt, electric conductivity titration, cement dispersing agent

1967-004
リグニンスルホン酸のゲル化に関する研究
秦邦男，中村孝一
東北パルプ株式会社
Studies on gelation of lignosulfonates
Kunio Hata, Koichi Nakamura
Tohoku Pulp Co., Ltd
Keywords: beech, *Fagus crenata*, sulfite cooking black liquor, gelation, dicyclohexylamine- n-butanol extraction, potassium dichromate

1967-005
亜硫酸パルプ排液と重クロム酸の反応に関する 2，3 の考察
岡部次郎，町原　晃，三浦義之
山陽パルプ株式会社
Reaction of sulfite spent liquor with dichromate
Jiro Okabe, Akira Machihara, Yoshiyuki Miura
Sanyo Pulp Co., Ltd.
Keywords: sulfite pulp, spent liquor, dichromate, soil stabilizer, lignosulfonic acid, gelation, chelate

1967-006
フェノール類の酸化的カップリング反応
熊野谿従、加藤　隆
東京大学工学部
Oxidative coupling reaction of phenolic compounds
Ju Kumanotani, Takashi Kato
Faculty of Engineering, the University of Tokyo

Keywords: quinone quinhydron, quinone methide, radical reaction

1967-007
リグニンモデル化合物と過酢酸との反応における側鎖の影響
鈴木金道[*1]、畠山兵衛[*2]、中野準三[*2]、右田伸彦[*2]
[*1] 東北パルプ株式会社、[*2] 東京大学農学部
Effect of side chain structure on the reaction of lignin model compounds with peracetic acid Kanemichi Suzuki[*1], Hyoe Hatakeyama[*2], Junzo Nakano[*2], Nobuhiko Migita[*2]
[*1]Tohoku pulp Co.Ltd., [*2]Faculty of Agriculture, the University of Tokyo.
Keywords: vanillyl alcohol, barium vanillyl sulfonate, vanillyl ethyl sulfide

1967-008
リグニンモデル化合物の過酢酸酸化分解について
沖　妙、木下良郎、石川久雄
愛媛大学農学部
Oxidation of lignin model compounds by peracetic acid
Tae Oki, Yosiro Kinoshita, Hisao Ishikawa
Faculty of Agriculture, Ehime University
Keywords: vanillyl alcohol, vanillin, guaiacylglycerol, isoeugenol, Baeyer-Villiger Reaction

1967-009
プロトリグニンの水素化分解に関する研究（第 2 報）1,2-Diaryl Propane 構造を有する分解物の単離
太田路一、榊原　彰
北海道大学農学部
Hydrogenolysis of protolignin (II), Isolation of 1,2-diaryl propane type products
Michikazu Ota, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: Yezo spruce, *Picea jezoensis*, paper chromatography, 1,2-bis-(4-hydroxy-3-methoxyphenyl)-propanol-3

1967-010
クラフトパルプの塩素による漂白について
寺島典二[*1]、篠田善彦[*2]、神田　孝[*1]
[*1] 名古屋大学農学部、[*2] 岐阜大学農学部
Bleaching of kraft pulp with chlorine
Noritsugu Terashima[*1], Yoshihiko Shinoda[*2], Takashi Kanda[*1]
[*1]Faculty of Agriculture, Nagoya University, [*2]Faculty of Agriculture, Gifu University
Keywords: vanillyl alcohol, quinhydron, stilbene, lignin-carbohydrate bond

1967-011
サルフアイト蒸解における着色構造の生成について
飯塚堯介、中野準三、右田伸彦
東京大学農学部
Formation of chromopholic structures during sulfite cooking
Gyosuke Meshitsuka, Junzo Nakano, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: red pine, *Pinus densiflora*, birch, *Betula maximowiczii*, lignin sulfonic acid, combined sulfur dioxide, catechol, hemicellulose

1967-012
リグニン中のラジカルの温度依存性
畠山兵衛、中野準三、右田伸彦
東京大学農学部
Temperature dependence of stability of radical in lignin

Hyoue Hatakeyama, Junzo Nakano, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: electron spin resonance, broad line nuclear magnetic resonance, milled wood lignin, dioxane lignin, lignin sulfonic acid

1967-013
樹皮の難溶性リグニンについて
十河村男、幡　克美
香川大学農学部
Low-solubility lignin in tree bark
Murao Sogo, Katsumi Hata
Faculty of Agriculture, Kagawa University
Keywords: red pine, *Pinus densiflora*, Yezo spruce, *Picea jezoensis*, *Acacia*, Japanese oak, *Quercus crispula*, *Quercus serrata*, chestnut, *Castanea crenata*, dioxane lignin

1967-014
MWL、LCC およびその抽出残渣リグニンの分解物における比較（第2報）
松倉紀男、榊原　彰
北海道大学農学部
Comparison of degradation products of MWL, LCC and lignin in extracted residue (II)
Motoo Matsukura, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: protolignin, potassium permanganate oxidation, nitrobenzene oxidation, ethanolysis, condensed structure

1967-015
リグニン樹脂発泡体製造に関する研究　—縮合に関する二，三の知見—
森　滋、阿部　勲、峯村伸哉、窪田　実
北海道林産試験場
Production of plastics form from lignin — Results obtained from cndensation test—
Shigeru Mori, Isao Abe, Shinya Minemura, Minoru Kubota
Hokkaido Forest Products Research Institute
Keywords: kraft lignin, formaldehyde, hydroxymethylated lignin

1967-016
チオリグニンのイソシアネート化について
戴　清華、沢登丈夫、中野準三、右田伸彦
東京大学農学部
Reaction of thiolignin with trilene diisocyanate
Seika Tai, Takeo Sawanobori, Junzo Nakano, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: urethane bond, allophanate bond, *m*-phenylenediamine, polyethyleneglycol

1967-017
リグニンと合成高分子化合物との共縮合に関する研究　—ポリメタアクロイルクロライドと諸種水酸基とのエステル化反応
内藤寿夫、福住俊郎、南　享二
東京大学農学部
Studies on the copolymerization of lignin with synthetic polymer —Esterification of several hydroxyl compounds with polymethacryloyl chloride
Hisao Naito, Toshio Fukuzumi, Kyoji Minami
Faculty of Agriculture, the University of Tokyo
Keywords: phenol, methoxyphenol, vanillyl alcohol, NMR spectra

1967-018

放射線の空気中前照射によるリグニンのグラフト化
村木永之介、越島哲夫
大阪工業技術試験所
Grafting of lignin with pre-radiation in the air
Einosuke Muraki, Tetsuo Koshijima
Osaka Institute of Advanced Industrial Science and Technology
red pine, *Pinus densiflora*, hydrochloric acid lignin, lignin sulfonic acid, styrene

1967-019
リグニンモデル化合物のアルカリ蓄電池に対する作用
林 晄、木下恭介
立命館大学理工学部
Effect of lignin models on alkali storage battery
Akira Hayashi, Kyosuke Kinoshita
College of Science and Engineering, Ritsumeikan University
Keywords: thiolignin, catechol, guaiacol, pyrogallol, maleic acid, chelate

1967-020
亜硫酸パルプ廃液活性炭について
岸本 定吉＊[1]、森 見二＊[2]
＊[1]東京教育大学農学部、＊[2]静岡大学農学部
Production of active carbon from sulfite waste liquor
Teikichi Kishimoto, Kenji Mori
＊[1]Faculty of Agriculture, Tokyo University of Education, ＊[2]Faculty of Agriculture, Shizuoka University
Keywords: activation by zinc chloride, water vapor activation

1967-021
フェニルプロパン誘導体のガスクロマトグラフィ
山口 彰、宮崎 信、高橋 敏
林業試験場
Gas chromatography of phenylpropane derivatives
Akira Yamaguchi, Makoto Miyazaki, Satoshi Takahashi
Forestry and Forest Products Research Institute
Keywords: trimethylsilylether, side-chain structure, side-chain hydroxyl group

1967-022
リグニンの電子スペクトルの解析
飯山賢治、中野準三、右田伸彦
東京大学農学部
Resolution of electronic spectra of lignin
Kenji Iiyama, Junzo Nakano, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: Yezo spruce, *Picea jezoensis*, milled wood lignin, lignin sulfonic acid, absorption band, guaiacyl nucleus, syringyl nucleus

1967-023
チオリグニンのポーラログラフ的研究（第 12 報）アルカリ蒸解中におけるクアヤシル核 5 位置換構造の生成について
玉生征人、寺島典二、神田 孝
名古屋大学農学部
Polarography of lignin (XII), Formation of substructure with substitution at 5 position of guaiacyl nucleus during alkali pulping
Masato Tamao, Noritsugu Terashima, Takashi Kanda
Faculty of Agriculture, Nagoya University

Keywords: red pine, *Pinus densiflora*, thiolignin, polarography, alkaline cooking, guaiacyl nucleus, condensed unit

1967-024
担子菌によるリグニンの分解における芳香族化合物添加の影響
原口隆英
東京農工大学農学部
Effect of addition of aromatic compounds on the degradation of lignin by basidiomycetes
Takafusa Haraguchi
Faculty of Agriculture, Tokyo University of Agriculture and Technology
Keywords: *Pycnoporus coccineus*, Yezo spruce, *Picea jezoensis*, benzoic acid, *p*-hydroxybenzoic acid, vanillic acid, ferulic acid

1967-025
木材腐朽菌の酵素によるリグニンの分解 —リグニンのアリルアルキルエーテル結合の分解
福住俊郎、南　享二
東京大学農学部
Degradation of lignin by enzyme of wood-rotting fungi, –Cleavage of arylalkyl ether bond
Toshio Fukuzumi, Kyoji Minami
Faculty of Agriculture, the University of Tokyo
Keywords: Yezo spruce, *Picea jezoensis*, *Perenniporia subacida*, veratrylglycerol-*β*-guaiacyl ether, laccase

1967-026
タケノコの木化における O-メチルトランスフエラーゼの役割について
樋口隆昌、島田幹夫、大橋英雄
岐阜大学農学部
Role of *O*-methyltransferase in lignification of bamboo shoot
Takayoshi Higuchi, Mikio Shimada, Hideo Ohashi
Faculty of Agriculture, Gifu University
Keywords: *Phyllostachys pubescens*, *Phyllostachys reticulata*, caffeic acid, S-adenosylmethionine, ferulic acid, sinapic acid

1967-027
タケノコの木化に伴う関連酵素の変動について
樋口隆昌、島田幹夫
岐阜大学農学部
Change of activity of enzymes involved in lignification of bamboo
Takayoshi Higuchi, Mikio Shimada
Faculty of Agriculture, Gifu University
Keywords: *Phyllostachys pubescens*, *Phyllostachys reticulata*, phenylalanine ammonia-lyase, peroxidase

第13回（1968.10.26-27）名古屋大学農学部

1968-001
リグニンのメトキシル基生成に関する生化学的研究
樋口隆昌[*1]、島田幹夫[*2]、大橋英雄[*2]
[*1]京都大学木材研究所、[*2]岐阜大学農学部
Biochemical study on the formation of methoxyl groups of lignin
Takayoshi Higuchi[*1], Mikio Shimada[*2], Hideo Ohashi[*2]
[*1] Wood Research Institute, Kyoto University, [*2] Faculty of Agriculture, Gifu University
Keywords: *Phyllostachys pubescens*, *Phyllostachys reticulata*, *Ginkgo biloba*, *Cryptomeria japonica*, *Podocarpus macrophyllus*, yew, *Taxus cuspidate*, autoradiography, *O*-methyltransferase

1968-002
稲科植物リグニン中の *p*-クマール酸のエステル結合に関する研究
樋口隆昌[*1]、島田幹夫[*2]、山崎　徹[*1]、福塚　哲[*2]
[*1]京都大学木材研究所、[*2]岐阜大学農学部
Studies on the *p*-coumaric ester bond of grass lignin
Takayoshi Higuchi[*1], Mikio Shimada[*2], Toru Yamasaki[*1], Tetsu Fukuzuka[*2]
[*1] Wood Research Institute, Kyoto University, [*2] Faculty of Agriculture, Gifu University
Keywords: bamboo, *Arundo donax*, *Coix*, *Phragmites*, DHP

1968-003
木材腐朽菌によるリグニンの分解
石原達夫、宮崎　信
林業試験場
Degradation of lignin by wood-rotting fungi
Tatsuo Ishihara, Makoto Miyazaki
Forestry and Forest Product Research Institute
Keywords: *Polyporus versicolor*, milled wood lignin, catechol, *Pseudomonas*

1968-004
樹皮リグニンの定量について
十河村男、幡　克美
香川大学農学部
Determination of lignin content in bark
Murao Sogo, Katsumi Hata
Faculty of Agriculture, Kagawa University
Keywords: Japanese red pine, *Pinus densiflora*, Yezo spruce, *Picea jezoensis*, *Quercus serrata*, chestnut, *Castanea crenata*, cork oak, Quercus variabilis*, Klason lignin, dioxane lignin*

1968-005
リグニンの親水性に関する研究
岡部次郎，工藤正邦
山陽パルプ株式会社
Studies on hydrophilicity of lignin
Jiro Okabe, Masakuni Kudo
Sanyo Pulp Co., Ltd.
Keywords: dioxane lignin, hydrophilicity, hygroscopy

1968-006
多段漂白における塩素化–アルカリ抽出（III）塩素化された DL の吸湿性について
河内　進策、武井　斎
宮崎大学農学部
Chlorination-alkali extraction in multistage bleaching (III), Hygroscopy of chlorinated dioxane lignin

Shinsaku Kawachi, Hitoshi Takei
Faculty of Agriculture, Miyazaki University
Keywords: red pine, *Pinus densiflora*, *Machilus thunbergii*, dioxane lignin

1968-007
可塑剤によるリグニンの可塑化について
坂田 功、青柳祥二、千手諒一
九州大学農学部
Plasticization of lignin by plasticizer
Isao Sakata, Shoji Aoyagi, Ryoichi Senju
Faculty of Agriculture, Kyusyu University
Keywords: red pine, *Pinus densiflora*, dioxane lignin, thiolignin, phthalic acid ester, tributyl phosphate, softening temperature

1968-008
チオリグニンの加熱時における活性基量の変化について
岩見田 紏，佐藤孝一郎
国策パルプ株式会社
Change in the amount of reactive groups during heat treatment of thiolignin
Tadashi Iwamida, Koichiro Sato
Kokusaku Pulp Co., Ltd.
Keywords: reactive groups, alcoholic hydroxyl group, phenolic hydroxyl group, carboxyl group

1968-009
リグニンラジカルの性状について
畠山兵衛[*1]、籏野 晃[*1]、中野準三[*2]、右田伸彦[*2]
[*1]アラスカパルプ株式会社、[*2]東京大学農学部
Properties of radical in lignin
Hyoe Hatakeyama[*1], Akira Hatano[*1], Junzo Nakano[*2], Nobuhiko Migita[*2]
[*1]Alaska Pulp Co. Ltd., [*2]Faculty of Agriculture, the University of Tokyo
Keywords: lignin model compounds, electron spin resonance spectra, milled wood lignin, dioxane lignin, calcium lignosulfonate, thiolignin, γ-ray irradiation

1968-010
リグニン分子中のピノレジノール構造について（第 5 報）酸アルカリ処理とピノレジノール構造
荻山紘一、近藤民雄
九州大学農学部
On the pinoresinol type of structural units in lignin molecule (V), Effect of acid or alkali treatment on pinoresinol structures
Koichi Ogiyama, Tamio Kondo
Faculty of Agriculture, Kyusyu University
Keywords: Japanese red pine, *Pinus densiflora*, *Cryptomeria japonica*, *Betula Tauschii*, *Shorea negrosensis*, dioxane lignin, symplocosigenol

1968-011
アルカリ処理によるリグニン分子の変化 —NMR による芳香環置換度の測定について
諸星紀幸、榊原 彰
北海道大学農学部
Change in lignin molecule by alkaline treatment, — Determination of condensed type unit by NMR spectroscopy
Noriyuki Morohoshi, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: Yezo spruce, *Picea jezoensis*, milled wood lignin, assignment of proton signal

1968-012
液安中金属ナトリウムによるリグニンの分解
山口　彰、広居忠量、宮崎　信
林業試験場
Degradation of lignin with metallic sodium in liquid ammonia
Akira Yamaguchi, Tadakazu Hiroi, Makoto Miyazaki
Keywords: Yezo spruce, *Picea jezoensis*, milled wood lignin, lignin carbohydrate complex, paper chromatography, gas chromatography

1968-013
プロトリグニンの水素化分解（第 4 報）フェニルクマラン開環型分解物の単離、同定について
松倉紀男、榊原　彰
北海道大学農学部
Hydrogenolysis of protolignin. IV. Isolation and identification of open-ring-phenylcoumaran type products
Motoo Matsukura, Akira sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: Yezo spruce, *Picea jezoensis*, thin-layer chromatography, gas chromatography, 1-(4-hydroxy-3-methoxyphenyl)-2-(2’-hydroxy-3’-methoxy-5’-propylphenyl)-propane

1968-014
ジオキサン-水によるリグニンの加水分解（第 8 報）
佐野嘉拓、榊原　彰
北海道大学農学部
Hydrolysis of lignin with dioxane and water (VIII)
Yoshihiro Sano, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: column chromatography, *p*-hydroxyphenylglycerol, NMR, UV absorption spectroscopy

1968-015
Björkman リグニンの酸素酸化に関する研究
渡辺貞良、林　治助、戸坂圀夫、小林昌子
北海道大学工学部
Oxidation of Björkman lignin with oxygen
Sadayoshi Watanabe, Jisuke Hayashi, Kunio Tosaka, Masako Kobayashi
Faculty of Engineering, Hokkaido University
Keywords: Yezo spruce, *Picea jezoensis*, functional group, hydroxyl group, carboxyl group, infrared absorption spectroscopy

1968-016
リグニンスルホン酸の電解酸化
小川博嗣、富田由明
東京工業試験所
カルボキシル基、メトキシル基
Electrolytic oxidation of lignin sulfonic acid
Hirotsugu Ogawa, Yoshiaki Tomita
Tokyo Institute of Advanced Industrial Science and Technology
Keywords: carboxyl group, methoxyl group,

1968-017
電子スペクトルの解析によるリグニンの着色機構の検討
飯山賢治、中野準三、右田伸彦
東京大学農学部
Studies on the coloring mechanism of lignin by the electronic spectral analysis
Kenji Iiyama, Junzo Nakano, Nobuhiko Migita

Faculty of Agriculture, the University of Tokyo
Keywords: thiolignin, milled wood lignin, lignin model compounds, adsorption band, vanillyl alcohol, assignment of absorption band

1968-018
リグニンに対する亜二チオン酸塩の反応機構について
細谷修二、畠山兵衛、中野準三、右田伸彦
東京大学農学部
Reaction mechanism of sodium hydrosulfite with lignin
Shuji Hosaya, Hyoe Hatakeyama, Junzo Nakano, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: calcium lignosulfonate, lignin model compounds, vanillin, acetoguaiacone, isoeugenol, *o*-quinone

1968-019
リグニン脱メチル生成物の着色について
林 晄、上北忠之
立命館大学理工学部
Coloring of demethylated lignin
Akira Hayashi, Tadayuki Kamikita
College of Science and Engineering, Ritsumeikan University
Keywords: guaiacol, 1-cyclopentene carboxylic acid, catechol, quinhydron, quinone

1968-020
サルファイト蒸解におけるリグニンの着色について
飯塚堯介、川上菊士、中野準三、右田伸彦
東京大学農学部
Coloring of lignin during sulfite cooking
Gyosuke Meshitsuka, Kikuo Kawakami, Junzo Nakano, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: fir, *Abies firma*, functional group, UV absorption difference spectroscopy

1968-021
Hydrotropic cooking について
村主信彦、近藤民雄
九州大学農学部
Studies on the hydrotropic cooking
Nobuhiko Suguri, Tamio Kondo
Faculty of Agriculture, Kyusyu University
Keywords: xylene sulfonic acid, toluene sulfonic acid, benzene sulfonic acid, benzoic acid, surface tension

1968-022
リグニンの蓄電池に及ほす効果について
林 晄，木下恭介
立命館大学理工学部
Effect of addition of lignin to battery
Akira Hayashi, Kyousuke kinoshita
College of Science and Engineering, Ritsumeikan University
Keywords: polyphenol, chelating agent, catechol, resorcinol

1968-023
リグノスルホン酸塩の色におよほす重金属イオンの影響
飯塚堯介、中野準三，右田伸彦
東京大学農学部

Effect of heavy metal ions on the color of lignosulfonate
Gyosuke Meshitsuka, Junzo Nakano, Nobuhiko Migita
Faculty of Agriculture, the University of Tokyo
Keywords: iron, copper, nickel, vanadium, manganese, chromium, visible light absorption spectra

1968-024
リグノスルホン酸類と各種金属イオンとの反応性
猪狩俶将，横山正一郎、室井和彦
東京工業試験所
Reactivity of various metal ions with lignosulfonic acid
Yoshimasa Ikari, Shoichiro Yokoyama, Kazuhiko Muroi
Tokyo Institute of Advanced Industrial Science and Technology
Keywords: iron, calcium, cadmium, nickel, copper, chromium, manganese, UV light absorption spectroscopy

1968-025
亜硫酸パルプ排液と重クロム酸の反応に関する研究（第2報）
岡部次郎，町原　晃，三浦義之
山陽パルプ株式会社
Reaction of sulfite spent liquor with dichromate (II)
Jiro Okabe, Akira Machihara, Yoshiyuki Miura
Sanyo Pulp Co., Ltd.
Keywords: soil stabilizer, lignosulfonic acid, sugar, gelation, chelate

1968-026
ポリフェノールの酸化カップリング反応
熊野谿従、加藤　隆
東京工業大学
Oxidative coupling reaction of polyphenols
Ju Kumanotani, Takashi Kato
Tokyo Institute of Technology
Keywords: urushiol, thin layer chromatography, *o*-quinone, nuclear magnetic resonance

1968-027
重クロム酸塩によるフェノールの酸化カップリング
田中浩雄、坂田　功、千手諒一
九州大学農学部
Oxidative coupling of phenols by potassium dichromate
Hiroo Tanaka, Isao Sakata, Ryoichi Senjyu
Faculty of Agriculture, Kyusyu University
Keywords: p-cresol, creosol, manganese

1968-028
リグニンのゲル化機構
田中浩雄、坂田　功、千手諒一
九州大学農学部
Gelation mechanism of lignin
Hiroo Tanaka, Isao Sakata, Ryoichi Senjyu
Faculty of Agriculture, Kyusyu University
Keywords: chromium, chelate, lignin sulfonic acid, polyhydroxystyrene sulfonic acid

第14回（1969.10.28-29）東京、日本化学会講堂

1969-001
アテ材リグニンの化学的特性に関する研究（第2報）
諸星紀幸、榊原　彰
北海道大学農学部
Chemical properties of of reaction wood (II)
Noriyuki Morohoshi, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: Abies mayriana, Fraxinus excelsissima*, milled wood lignin, lignin carbohydrate complex, potassium permanganate oxidation, ethanolysis, nitrobenzene oxidation, gas chromatography*

1969-002
ジオキサン一水によるリグニンの加水分解（第9報）
佐野嘉拓、榊原　彰
北海道大学農学部
Hydrolysis of lignin with dioxane and water (IX)
Yoshihiro Sano, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: guaiacylglycerol, 1,2-bisguaiacylpropane1,3-diol, NMR, mass spectrometry

1969-003
AP法廃液からのアルカリ・リグニンの性状について
香川詔士、内田　壮
関東学院大学工学部
Characteristics of alkali lignin in soda pulping waste liquor
Shoji Kagawa, So Uchida
Faculty of Engineering, Kanto Gakuin University
Keywords: larch, *Larix Kaempferi*, soda pulping waste liquor, hydrochloric acid lignin, differential thermal analysis, nitrobenzene oxidation

1969-004
クラフト蒸解中におけるグアヤシル核5位置換型構造の生成について
玉生征人、寺島典二
名古屋大学農学部
Formation of guaiacyl nucleus with substitution at position 5 during kraft pulping
Masato Tamao, Noritsugu Terashima
Faculty of Agriculture, Nagoya University
Keywords: ^{14}C-labeled lignin model compounds, guaiacylglycerol-β-guaiacyl ether-[α-^{14}C], guaiacylglycerol-β-guaiacyl ether-[β-^{14}C], guaiacylglycerol-β-guaiacyl ether-[γ-^{14}C],

1969-005
リグニン中のピノレジノール構造について（第6報）KP蒸解とピノレジノール構造との関係
荻山紘一、谷口栄一
山形大学農学部
Pinoresinol structure in lignin (VI), Behavior of pinoresinol structure during kraft cooking
Koichi Ogiyama, Eichi Taniguchi
Faculty of Agriculture, Yamagata University
Keywords: *Symplocos lucida*, *Pinus densiflora*, *Betula tauschii*, symplocosin, symplocosigenol, syringaresinol

1969-006
リグノスルホン酸塩中の共役二重結合について
飯塚堯介、中野準三

東京大学農学部
Conjugated double bonds in lignosulfonate
Gyosuke Meshitsuka, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: coniferaldehyde, coniferyl alcohol, stilbene, chalcone, phenylcoumaran

1969-007
リグニン分解木材腐朽菌（未同定菌）によるアセトン・リグニンの分解生成物
福住俊郎、南　享二
東京大学農学部
Degradation products of acetone lignin by a wood-rotting fungus (unidentified white rot type)
Toshio Fukuzumi, Kyoji Minami
Faculty of Agriculture, the University of Tokyo
Keywords: Yezo spruce, *Picea jezoensis*, jar-fermentor, hydroxymatairesinol

1969-008
カワラタケ酵素のワニリン酸に対する挙動
石原達夫、宮崎　信
林業試験場
Behavior of enzyme of *Polyporus versicolor* on vanillic acid
Tatsuo Ishihara, Makoto Miyazaki
Forestry and Forest Product Research Institute
Keywords: laccase, peroxidase, UV spectroscopy, IR spectroscopy, NMR

1969-009
広葉樹の葉における芳香核構造の季節的変動
田中治郎、千野広子
林業試験場
Seasonal change of aromatic structures in the leaves of hardwood
Jiro Tanaka, Hiroko Chino
Forestry and Forest Product Research Institute
Keywords: sycamore, *Platanus occidentalis*, nitrobenzene oxidation, formation of aldehydes

1969-010
Hydrotropic Cooking について（II）
村主信彦、近藤民雄
九州大学農学部
Hydrotropic cooking (II)
Nobuhiko Suguri, Tamio kondo
Faculty of Agriculture, Kyusyu University
Keywords: sodium xylenesulfonate, sodium benzoate, gel filtration chromatography

1969-011
リグニンの水溶性化に関する研究
工藤正邦，岡部次郎
山陽パルプ株式会社
Studies on water solubilization of lignin
Masakuni Kudo, Jiro Okabe
Sanyo Pulp Co., Ltd.
Keywords: solubilization, dioxane lignin, sulfonation, hygroscopy, sulfonic group

1969-012
ゲル濾過法によるリグノスルホン酸類の分別
猪狩俶将、横山正一郎

東京工業試験所
Fractionation of lignosulfonic acids by gel filtration chromatography
Yoshimasa Ikari, Shoichiro Yokoyama
Tokyo Institute of Advanced Industrial Science and Technology
Keywords: molecular weight distribution, sephadex, affinity

1969-013
リグノスルホン酸とスチレンのグラフト共重合における Fe[III]イオンによる酸化の効果
村木永之介、越島哲夫
大阪工業技術試験所
Effect of oxidation with ferric ion on the copolymerization of lignosulfonic acid and styrene
Einosuke Muraki, Tetsuo Koshijima
National Industrial Research Institute of Osaka
Keywords: vanillyl sulfonic acid, graft polymer

1969-014
フエノール系高分子（リグニンモデル）の合成とその重クロム酸塩によるゲル化
田中浩雄、坂田　功、千手諒一
九州大学農学部
Synthesis of phenolic polymers (lignin model) and their gelation by dichromate
Hiroo Tanaka, Isao Sakata, Ryoichi Senju
Faculty of Agriculture, Kyusyu University
Keywords: poly-4-hydroxystyrenesulfonic acid, poly-4-hydroxy-3-methoxystyrene sulfonic acid, poly-4-hydroxy-3,5-dimethoxystyrene sulfonic acid, viscosity, molecular weight

1969-015
リグニンゲルとポリウロン酸ゲルの粘性について
石川久雄、木下良郎、大久保克美、沖　妙
愛媛大学農学部
Viscosity of lignin gel and polyuronide gel
Hisao Ishikawa, Yoshiro Kinoshita, Katsumi Okubo, Tae Oki
Faculty of Agriculture, Ehime University
Keywords: *Abelmoschus manihot*, alginate, lignin sulfonic acid, calcium ion

1969-016
ベラトリルスルホン酸の電解酸化
小川博嗣、戸倉保司
東京工業試験所
Electrolytic oxidation of veratryl sulfonic acid
Hiroshi Ogawa, Yasusi Tokura
National Industrial Research Institute of Tokyo
Keywords: pH, UV absorption spectra, demethylation

1969-017
チオリグニンの熱重合時における生成ガスについて
岩見田　糺
国策パルプ株式会社
Gases generated during polymerization of thiolignin by heat treatment
Tadashi Iwamida
Kokusaku Pulp Co., Ltd.
Keywords: heat treatment, polymerization, gaschromatography

1969-018
リグニンの DSC による熱解析

畠山兵衛、久保田勝也
製品科学研究所
Thermal analysis of lignin by differential scanning calorimetry
Hyoe Hatakeyama, Masaya Kubota
Industrial Products Research Institute
Keywords: glass transition temperature, differential scanning calorimetry, milled wood lignin, dioxane lignin, thiolignin, calcium lignosulfonate

1969-019
リグニンモデル化合物の過酢酸酸化分解について
沖　妙、木下良郎、石川久雄
愛媛大学農学部
Oxidative degradation of lignin model compounds by peracetic acid
Tae Oki, Yoshiro Kinoshita, Hisao Ishikawa
Faculty of Agriculture, Ehime University
Keywords: Baeyer-Villiger reaction, dehydrodiisoeugenol, isoeugenol, UV absorption spectroscopy

1969-020
パルプ廃液の色に関する研究（I）KP 晒廃液の色とオキシリグニン
鮫島一彦、近藤民雄
九州大学農学部
Studies on the color of pulping waste liquor (I), Color of waste liquor from kraft pulp bleaching and oxylignin
Kazuhiko Sameshima, Tamio Kondo
Faculty of Agriculture, Kyusyu University
Keywords: Japanese red pine, *Pinus densiflora*, *Betula Tauschii*, multistage bleaching, UV absorption spectroscopy

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1970-001
タケリグニンのメトキシル基生成に関する生化学的研究
島田幹夫、樋口隆昌
京都大学木材研究所
Biochemical studies on the formation of methoxyl groups in bamboo lignin
Mikio Shimada, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: *Phyllostachys reticulata*, bamboo shoot, *O*-methyltransferase, caffeic acid-2-^{14}C, ferulic acid-2-^{14}C, *S*-adenosyl methionine

1970-002
タケ及びイネ科植物リグニン中の *p*–クマール酸エステル結合に関する研究
島田幹夫、樋口隆昌
京都大学木材研究所
Studies on the coumaric acid ester bonds in lignins of bamboo and gramineous plants
Mikio Shimada, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: dehydrogenative polymer, coniferyl alcohol, UV absorption spectra, radio-labeled *p*-coumaric acid, methanolysis

1970-003
コニフェリルアルコールの脱水素重合におよばすヘミセルロースの影響
樋口隆昌、荻野桂作
京都大学木材研究所
Effect of hemicelluloses on dehydrogenative polymerization of coniferyl alcohol
Takayoshi Higuchi, Keisaku Ogino
Wood Research Institute, Kyoto University
Keywords: pectin, peroxidase, dehydrogenative polymer, molecular weight, UV absorption spectra

1970-004
酵素によるリグニンのエーテル結合の分解
松本　久、福住俊郎、南　享二
東京大学農学部
Cleavage of ether bonds in lignin by enzyme
Hisashi Matsumoto, Toshiro Fukuzumi, Kyoji Minami
Faculty of Agriculture, the University of Tokyo
Keywords: wood rotting fungi, *Perenniporia subacida*, thin layer chromatography, gas chromatography

1970-005
放線菌の一種によるリグニンの分解
原口隆英
東京農工大学農学部
Degradation of lignin by *Actinomycetes* sp.
Takafusa Haraguchi
Faculty of Agriculture, Tokyo University of Agriculture and Technology
Keywords: potassium lignosulfonate, vanillic acid, UV absorption spectrometry, chemical oxygen demand

1970-006
ヒノキ-MWL 及び LCC の化学特性、その分子量分布について
広居忠量、宮崎　信
林業試験場

Chemical properties of MWL and LCC of Japanese cypress, and their molecular weight distribution
Tadakazu Hiroi, Makoto Miyazaki
Forestry and Forest Products Research Institute
Keywords: Japanese cypress, *Chamaecyparis obtusa,* gel permeation chromatography, number average molecular weight, vapor pressure osmometry

1970-007
液安中の金属ナトリウムによるリグニンの分解（II）
山口 彰、宮崎 信
林業試験場
要旨なし（中止）

1970-008
サルファイト蒸解過程におけるリグニンの酸加水分解について
飯塚尭介、中野準三
東京大学農学部
Acid hydrolysis of lignin during sulfite cooking process
Gyosuke Meshitsuka, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: red pine, *Pinus densiflora*, repeating unit, lignosulfonic acid, molecular weight distribution, ge filtration chromatography

1970-009
塩化アルミニウムによるリグノスルホン酸塩の凝集沈澱について
飯塚尭介、徐道太郎、中野準三
東京大学農学部
Precipitation of lignisulfonate by coagulation with aluminum chloride
Gyosuke Meshitsuka, Michitaro Jo, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: softwood, conifer, gel filtration, pH, phenolic hydroxyl group, alcoholic hydroxyl group

1970-010
リグノスルホン酸塩とメタクリル酸メチルのフエントン試薬によるグラフト重合反応（その 1）
南正院、斉藤雅康、村木永之介、越島哲夫
大阪工業技術試験所
Graft polymerization of lignosulfonate and methyl methacrylates by Fenton’s reagent (I)
Zeong-Woun Nam, Masayasu Saito, Einosuke Muraki, Tetsuo Koshijima
Osaka Institute of Advanced Industrial Science and Technology
Keywords: softwood, conifer, molecular weight, veratryl sulfonic acid *p*-hydroxybenzylsulfonic acid

1970-011
木材パルプのアクリルアミドグラフト重合にたいするリグニンの影響
小林晃夫*1、W. Brown*2、V. Stannett*3
*1国策パルプ株式会社、*2Uppsala 大学、*3North Carolina 州立大学
Influence of lignin on graft polymerization of acrylamide to wood pulp
Akio Kobayashi*1, W. Brown*2, V. Stannett*3
*1Kokusaku Pulp Co., Ltd., *2Uppsala University, *3North Carolina State University
Keywords: spruce, *Picea engelmannii*, KP, kraft pulp, BKP, bleached kraft pulp, DP, dissolve pulp, GP, ground wood pulp, cotton linter, electron spin resonance spectroscopy

1970-012
二、三のリグニンモデル化合物合成の試み ―グアヤシルプロペン類の合成―
福住俊郎、小宅茂夫、南 享二
東京大学農学部

Synthesis of a few lignin model compounds, –Synthesis of guaiacyl propenes-
Toshio Fukuzumi, Shigeo Koyake, Kyoji Minami
Faculty of Agriculture, the University of Tokyo
Keywords: guaiacyl vinyl ketone, vanilloyl acetoaldehyde, coniferyl alcohol

1970-013
次亜塩素酸ナトリウムによるリグニンモデル化合物の反応について
細谷修二、中野準三
東京大学農学部
Reaction of lignin model compounds with sodium hypochlorite
Shuji Hosaya, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: pH, vanillyl alcohol, veratryl alcohol, gaschromatography

1970-014
リグニンスルホン酸の二酸化塩素による酸化　—モデル化合物の酸化反応
中村孝一、横田金吾、秦　邦男
十条製紙株式会社
Oxidation of lignosulfonates with chlorine dioxide – Oxidation of model compounds
Koichi Nakamura, Kingo Yokota, Kunio Hata,
Jyujo Pulp Co., Ltd.
Keywords: lignosulfonates, chlorine dioxide, vanillyl sulfonate, syringyl sufonate

1970-015
2-(2-Methoxy-phenoxy)-1-(4-hydroxy-3-methoxyphenyl)-ethanol の過酢酸酸化について
沖　妙、大久保克美、石川久雄
愛媛大学農学部
Oxidation of 2-(2-methoxy-phenoxy)-1-(4-hydroxy-3-methoxyphenyl)-ethanol by peracetic acid
Tae Oki, Katsumi Okubo, Hisao Ishikawa
Faculty of Agriculture, Ehime University
Keywords: Baeyer-Villiger reaction, paper chromatography, UV absorption chromatography

1970-016
パルプ廃液の色に関する研究（II）塩素オキシリグニンの着色について
鮫島一彦、近藤民堆
九州大学農学部
Studies on the color of pulping waste liquor (II), On the color of chlorin-oxylignin
Kazuhiko Sameshima, Tamio Kondo
Faculty of Agriculture, Kyusyu University
Keywords: Pinus densiflora, Betula Tauschii, *oxylignin, pH dependence, functional groups*

1970-017
ハイドロトロピツク蒸解におけるリグニンの可溶化
石川久雄、沖　妙、大久保克美
愛媛大学農学部
Solubilization of lignin during hydrotropic cooking
Hisao Ishikawa, Tae Oki, Katsumi Okubo
Faculty of Agriculture, Ehime University
Keywords: beech, *Fagus crenata*, sodium *m*-xylenesulfonate, dioxane lignin, sodium salicilate

1970-018
Hydrotropic Cooking について（III）より強力なハイドロトロピック剤へのアプローチ
山田洋三、近藤民雄
九州大学農学部

Hdrotropic cooking (III), Approach toward more effective hydrotropic reagent
Yozo Yamada, Tamio Kondo
Faculty of Agriculture, Kyusyu University
Keywords: sodium salycilate, sodium aminobenzene sulfonate, viscosity

1970-019
アルカリ蒸解における酸素と硫黄の役割
飯山賢治、中山忠光、中野準三
東京大学農学部
Role of oxygen and sulfur in alkaline cooking
Kenji Iiyama, Tadamitsu Nakayama, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: lignin model compounds, vanillyl alcohol, acetoguaiacone, creosol, soda cooking, kraft cooking

1970-020
リグニンの脱メチル反応について
林 晄、谷口 彰
立命館大学理工学部
Demethylation reaction of lignin
Akira Hayashi, Akira Taniguchi
College of Science and Engineering, Ritsumeikan University
Keywords: *Pinus densiflora*, dioxane lignin, soda cooking, *o*-quinone

1970-021
リグニンのメチロール化反応について
阿部 勲、窪田 実
北海道林産試験場
Introduction of methylol groups onto lignin
Isao Abe, Minoru Kubota
Hokkaido Forest Products Research Institute
Keywords: kraft lignin, formaldehyde, vanillic acid, ferulic acid, *p*-coumaric acid

1970-022
チオリグニンの鋳型への利用
岩見田糺、佐藤孝一郎
国策パルプ株式会社
Utilization of thiolignin for shell mold
Tadashi Iwamida, Kouichiro Sato
Kokusaku Pulp Co., Ltd.
Keywords: hell mold, sand, binder, phenol

1970-023
アルカリリグニンからバニリンの製造について
香川詔士、六川真佐行. 堀井淑子
関東学院大学工学部
Production of vanillin from alkali lignin
Shoji Kagawa, Masayuki Mutsukawa, Toshiko Horii
Faculty of Engineering, Kanto Gakuin University
Keywords: larch, *Larix Kaempferi*, nitrobenzene oxidation, air oxidation, UV absorption spectroscopy

1970-024
バニリン製造における副生リグニンの性状について
品川和夫、工藤正邦
山陽パルプ株式会社

Properties of residual lignin during production of vanillin
Kazuo Shinagawa, Masakuni Kudo
Sanyo Pulp Co., Ltd.
Keywords: sulfite pulp, spent liquor, vanillin, by-product, chemical structure

1970-025
蓄電池添加剤としてのリグニンの効果
木下恭介、林 晄
立命館大学理工学部
Effect of lignin as lead-acid battery additive
Kyousuke kinoshita, Akira Hayashi
College of Science and Engineering, Ritsumeikan University
Keywords: polyphenol, novolac type phenolic resin, poly-4-hydroxy-3-methoxystyrene

第16回（1971.11.4-5）高松電機ビル

1971-001
植物体に投与されたフエルラ酸のデメトキシ、およびメトキシレーションに関する研究
島田幹夫、伏木秀文、樋口隆昌
京都大学木材研究所
Studies on the demethoxylation and methoxylation of ferulic acid fed to a plant
Mikio Shimada, Hidefumi Fushiki, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: *Phyllostachys pubescens*, sinapic acid, 5-hydroxyferulic acid, guaiacyl nucleus, syringyl nucleus, hardwood, softwood

1971-002
広葉樹、および針葉樹リグニンのメトキシル基形成に関する比較生化学的研究
島田幹夫、伏木秀文、樋口隆昌
京都大学木材研究所
Comparative biochemical studies on the formation of methoxyl groups in hardwood and softwood lignins
Mikio Shimada, Hidefumi Fushiki, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: *Phyllostachys pubescens*, *Pinus Thunbergii*, *Ginkgo biloba*, *O*-methyltransferase, *S*-adenosylmethionine

1971-003
ポプラリグニン中のパラハイドロキシ安息香酸の生合成
寺島典二, 森　勇
名古屋大学農学部
Biosynthesis of *p*-hydroxybenzoic acid in poplar lignin
Noritsugu Terashima and Isamu Mori
Faculty of Agriculture, Nagoya University
Keywords: *Populus nigra* x *Populus Maximowiczii*, phenylalanine ammonia-lyase, *t*-cinnamic acid, *p*-coumaric acid

1971-004
広葉樹リグニン生合成についての一考察
寺沢　実、古賀卓哉、奥山　寛、三宅基夫
帯広畜産大学
Studies on the biosynthesis of lignin in hardwood
Minoru Terasawa, Takuya Koga, Hiroshi Okuyama, Motoo Miyake
Obihiro University of Agriculture and Veterinary Medicine
Keywords: *Larix Kaempferi*, *Magnolia obobata*, *p*−glucocoumaryl alcohol, coniferin, syringin, cambial sap, softwood, hardwood

1971-005
MWL, LCC の磨砕に対する挙動
広居忠量、宮崎　信
林業試験場
Behavior of MWL and LCC during milling
Tadakazu Hiroi, Makoto Miyazaki
Government Forest Experiment Station
Keywords: *Chamaecyparis obtusa*, glucomannan, ball mill, IR spectra, molecular weight distribution

1971-006
種子リグニンの特性
萩山紘一、畠山隆一、故　谷口栄一

山形大学農学部
Characteristic properties of lignin in seeds
Koichi Ogiyama, Ryuuichi Hatakeyama, the late Eiichi Taniguchi
Faculty of Agriculture, Yamagata University
Keywords: *Pinus densiflora*, *Juglans Sieboldiana*, UV spectra, IR spectra, nitrobenzene oxidation

1971-007
竹リグニンのアシドリシス (第 2 報) アシドリシス生成物の分離同定
中坪文明、棚橋光彦、樋口隆昌
京都大学木材研究所
Acidolysis of bamboo lignin (II), Isolation and identification of acidolysis products
Fumiaki Nakatsubo, Mitsuhiko Tanahashi, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: gel filtration, NMR, IR, *p*-coumaric acid, arylglycerol-β-aryl ether substructure

1971-008
竹リグニンのアシドリシス（第 3 報）アリルグリセロール-β-アリルエーテルの合成とそのアシドリシス
樋口隆昌、棚橋光彦、中坪文明
京都大学木材研究所
Acidolysis of bamboo lignin (III), Synthesis of arylglycerol-β-aryl ether and its acidolysis
Takayoshi Higuchi, Mitsuhiko Tanahashi, Fumiaki Nakatsubo
Wood Research Institute, Kyoto University
Keywords: *Phyllostachys pubescens*, model compounds, acidolysis in dioxane-water

1971-009
プロトリグニンの水素化分解に関する研究（第 9 報） 新 2，3 量体の単離・同定について
松倉紀男[*1]、榊原　彰[*2]
[*1]十條製紙株式会社，[*2]北海道大学農学部
Hydrogenolysis of protolignin (IX), Isolation and identification of new dimeric and trimeric products
Motoo Matsukura[*1], Akira Sakakibara[*2],
[*1]Jujo Paper Co. Ltd., [*2]Faculty of Agriculture, Hokkaido University
Keywords: NMR, jezo spruce, *Picea jezoensis*, paper chromatography, thin-layer chromatography,

1971-010
リグニン-炭水化物複合体に関する研究　—ジオキサン−水による加水分解物からの単離—
武山浩武、榊原　彰
北海道大学農学部
Studies on the lignin-carbohydrate complex. —Isolation from hydrolysis products with dioxane-water
Hirotake Takeyama, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: *Picea jezoensis*, paper chromatography, thin-layer chromatography

1971-011
NMR を用いた MWL の測定
佐藤　惺、北村晃子、樋口隆昌
京都大学木材研究所
NMR analysis of MWL
Akira Sato, Teruko Kitamura, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: *Metasequoia glyptostroboides, Fagus crenata*, *Phyllostachys*, molecular weight distribution

1971-012
チオリグニンの熱的性質に及ぼす分子量の影響について
岩下建二[*1]、飯塚堯介[*1]、畠山兵衛[*2]、中野準三[*1]

[1] 東京大学農学部、[2]製品科学研究所
Effect of molecular weight on thermal properties of thiolignin
Kenji Iwashita*[1], Gyosuke Meshitsuka*[1], Hyoe Hatakeyama*[2], Junzo Nakano*[1]
*[1]Faculty of Agriculture, the University of Tokyo *[2]Industrial Products Research Institute
Keywords: *Abies mayriana*, *Fagus crenata,* gel filtration, differential scanning calorimetry

1971-013
リグニンモデル化合物の酸化電位について
小川博嗣
東京工業試験所
Oxidation potential of lignin model compounds
Hirotsugu Ogawa
Government Chemical Industrial Research Institute, Tokyo
Keywords: polarography, vanillin, vanillic acid, vanillyl sulfonic acid

1971-014
サルファイト蒸解におけるリグニン・糖複合体の挙動について
飯塚堯介、白銀英明、中野準三
東京大学農学部
Behavior of lignin-carbohydrate complex during sulfite cooking
Gyosuke Meshitsuka, Hideaki Shirogane, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: *Pinus densiflora*, gel filtration, peracetic acid treatment

1971-015
サルファイト系高歩留りパルプ製造時のリグニンの挙動
岩見田 紀*[1], 浜田忠平*[1], 李 宗藩*[2], 中野準三*[2]
*[1] 国策パルプ株式会社, *[2] 東京大学農学部
Behavior of lignin during sulfite chemimechanical pulping
Tadashi Iwamida*[1], Tadahira Hamada*[1], Sohan Ri*[2], Junzo Nakano*[2]
*[1]Kokusaku Pulp Co., Ltd., *[2]the University of Tokyo, Faculty of Agriculture
Keywords: defibration, sulfonic acid group, middle lamella, secondary wall

1971-016
クラフト蒸解における残存および溶出リグニンの性状
飯山賢治、中野準三
東京大学農学部
Properties of dissolved and residual lignin in kraft pulp
Kenji Iiyama, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: *Pseudotsuga taxifolia,* color of lignin, color of pulp, MWL, molecular weight distribution

1971-017
ソーダ蒸解によるリグニンの着色機構
林 晄、木下恭介、谷口 彰
立命館大学理工学部
Coloring mechanism of lignin during soda cooking
Akira Hayashi, Kyosuke Kinoshita, Akira Taniguchi
Faculty of Science and Engineering, Ritsumeikan University
Keywords: model compound, quinone, catechol, chromophoric groups

1971-018
2-(2-Methoxy-phenoxy)-1-(4-hydroxy-3-methoxyphenyl)-ethanol とそのメチル化物の過酢酸酸化について
沖 妙、大久保克美、石川久雄

愛媛大学農学部
Peracetic acid oxidation of 2-(2-Methoxy-phenoxy)-1-(4-hydroxy-3-methoxyphenyl)–ethanol
Tae Oki, Katsumi Okubo, Hisao Ishikawa
Faculty of Agriculture, Ehime University
Keywords: TLC, NMR, IR absorption spectroscopy

1971-019
β-アリルエーテル型リグニンモデル化合物の過酢酸酸化
坂井克己[*1]、黒田健一[*1]、岸本定吉[*2]
[*1]九州大学農学部, [*2]東京教育大学農学部
Peracetic acid oxidation of β-aryl ether type lignin model compounds
Kokki Sakai[*1], Ken-ichi Kuroda[*1], Sadakichi Kishimoto[*2]
[*1]Faculty of Agriculture, Kyushu University, [*2]Faculty of Agriculture, Tokyo University of Education
Keywords: conifer lignin, guaiacylglycerol-β-guaiacyl ether, gas chromatography, mass spectrometry

1971-020
酸化漂白剤によるビフエニル型リグニンモデル化合物の反応について
細谷修二、中野準三
東京大学農学部
Reaction of biphenyl type lignin model compounds with oxidative bleaching agents
Shuji Hosoya, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: dehydrodivanillyl alcohol, dehydrodiveratryl alcohol, sodium hypochlorite, hydrogen peroxide

1971-021
高歩留パルプの漂白機構について—漂白剤添加量と白色度増加との関係
加納 直[*1], 細谷修二[*2], 中野準三[*2]
[*1] 国策パルプ, [*2] 東京大学農学部
Mechanism of bleaching of high yield pulp – Relation between dosage of bleaching agent and increase of brightness
Tadashi Kano[*1], Shuji Hosoya[*2], Junzo Nakano[*2]
[*1]Kokusaku Pulp Co.,Ltd., [*2]Faculty of Agriculture, the University of Tokyo
Keywords: chemimechanical pulp, cold soda process, hydrogen peroxide, MWL

1971-022
塩素化リグニンのアルカリ抽出におよぼす熱処理の影響について(II)
河内進策
宮崎大学農学部))
Effect of thermal treatment on alkali extraction of chlorinated lignin (II)
Shinsaku Kawachi
Faculty of Agriculture, Miyazaki University
Keywords: *Pinus densiflora*, dioxane lignin, holocellulose

1971-023
ゲルろ過法による針葉樹と広葉樹リグノスルホン酸類の比較
猪狩俶将、横山正一郎
東京工業試験所
Comparison of lignosulfonic acids prepared from softwood and hardwood by gel filtration
Government Chemical Industrial Research Institute, Tokyo
Yoshimasa Ikari, Shoichirou Yokoyama
Keywords: sephadex

1971-024
リグノスルホン酸塩とメタクリル酸メチルのフエントン試薬によるグラフト重合反応(その 2)

越島哲夫、南　正院、村木永之介
大阪工業技術試験所
Graft copolymerization of methyl methacrylate onto lignosulfonate by Fenton reagent, II.
Tetsuo Koshijima, Chongwon Nam, Einosuke Muraki,
Government Industrial Research Institute, Osaka
Keywords: barium *p*-hydroxybenzylsulfonate, barium vanillylsulfonate, barium veratrylsulfonate,

1971-025
金属酸化物触媒の存在下におけるリグニンスルホン酸塩のアルカリ酸化分解　—酸化銅触媒の表面特性がバニリン生成反応に及ほす影響
高橋英郎、渡辺昭雄
東京工業試験所
Alkaline oxidative degradation of lignosulfonate in presence of metal oxide catalyst, —Effect of surface properties of copper oxide catalyst on vanillin production
Hideo Takahashi, Akio Watanabe
Government Chemical Industrial Research Institute, Tokyo
Keywords: volatile acid, oxygen consumption

1971-026
アルカリリグニンの空気酸化について
香川詔士、古梶　誠
関東学院大学工学部
Air oxidation of alkali lignin
Shoji Kagawa, Makoto Kokaji
Faculty of Engineering, Kanto Gakuin University
Keywords: *Larix Kaempferi*, gas chromatography

1971-027
バニリン製造における副生リグニンの性状に関する研究（第 2 報）
品川和夫，工藤正邦，岡部次郎
山陽パルプ
Properties of residual lignin during production of vanillin (II)
Kazuo Shinagawa, Masakuni Kudo, Jiro Okabe
Sanyo Pulp Co., Ltd.
Keywords: sulfite pulp, spent liquor, vanillin, by-product, lignin, molecular weight, sulfopropylation

1971-028
濃縮 SP 廃液とフエノールによる耐水性接着剤の製造に関する研究
榊原　彰、佐野嘉拓
北海道大学農学部
Preparation of water resistant adhesives from concentrated sulfite waste liquor and phenol
Akira Sakakibara, Yoshihiro Sano
Faculty of Agriculture, Hokkaido University
Keywords: chest nut powder, formaldehyde

1971-029
カワラタケのラッカーゼによる MWL の分解
石原達夫、宮崎　信
林業試験場
Degradation of MWL by laccase of *Polyporus versicolor*
Tatsuo Ishihara, Makoto Miyazaki
Forestry and Forest Product Research Institute
Keywords: *Acer palmatum* Thunb, wood rotting fungi, milled wood lignin, GPC

1971-030
加水分解酵素によるリグニンの分解
福住俊郎、南　享二
東京大学農学部
Degradation of lignin by hydrolase
Toshio Fukuzumi, Kyoji Minami
Faculty of Agriculture, the University of Tokyo
Keywords:	*Picea jezoensis, Polystictus sanquineus, Perenniporia subacida*, Brauns's lignin

1971-031
放線菌によるリグニンの分解（第 2 報）
原口隆英、諸星紀幸
東京農工大学農学部
Degradation of lignin by *Actinomycetes* (II)
Takafusa Haraguchi, Noriyuki Morohoshi
Faculty of Agriculture, Tokyo University of Agriculture and Technology
Keywords:	lignosulfonic acid, gel filtration, UV absorption spectra, *p*-hydoxybenzoic acid, vanillic acid

1971-032
パルプ廃液の色に関する研究（II）塩素化オキシリグニンの着色について（2）
鮫島一彦、住本昌之、近藤民雄
九州大学農学部
Studies on the color of pulping waste liquor (II)　Color of chlorinated oxylignin (2)
Kazuhiko Sameshima, Masashi Sumimoto, Tamio Kondo
Faculty of Agriculture, Kyushu University
Keywords:	benzoquinone, auxochrome, complex chromophore

1971-033
パルプ製造排水の凝集処理に関する研究
徐道太郎、飯塚堯介、中野準三
東京大学農学部
Treatment of pulp and paper mill wastewater by coagulation–flocculation
Michitaro Jo, Gyosuke Meshitsuka, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords:	lignosulfonate, chlorine treatment, alkali treatment, gel filtration

1971-034
パルプ廃水の清水化に関する研究　—クラフトリグニンの活性炭による吸着
壁谷　洋、藤井利郎、久保隆昌
四国工業技術試験所
Purification of pulp and paper mill wastewater – Adsorption of kraft lignin by activated carbon
Hiroshi Kabeya, Toshirou Fujii, Takamasa Kubo
Government Industrial Research Institute, Shikoku
Keywords:	adsorption isotherm

第17回（1972.11.4-5）京都大学農学部

1972-001
広葉樹材生長過程における S/V 比の変動
田中治郎、宮崎　信
林業試験場
Variation of S/V ratio during growing of hardwood
Jiro Tanaka, Makoto Miyazaki
Government Forest Experiment Station
Keywords: *Platanus occidentalis*, nitrobenzene oxidation

1972-002
加水分解酵素による木粉よりのリグニン分解物
福住俊郎
東京大学農学部
Degradation products from lignin in wood meal by hydolase
Toshiro Fukuzumi
Faculty of Agriculture, the University of Tokyo
Keywords: *Picea jezoensis*, cellulase from *Trametes sanquineus,* Meicelase

1972-003
南洋材リグニンの特性について（2）南洋材広葉樹の 1%−NaOH 易溶性リグニンについて
荻山紘一、安江保民
山形大学農学部
Characteristics of the tropical wood lignins (II), Lignin soluble in 1% NaOH in tropical hardwood
Koichi Ogiyama, Moritami Yasue
Faculty of Agriculture, Yamagata University
Parashorea melaanonan, Shorea rubroshorea, white lauan, red lauan, 1%NaOH-extract, polymer

1972-004
リグニンの水素化分解に関する研究（第 10 報）新二，三量体の単離について
須藤賢一、榊原　彰
北海道大学農学部
Hydrogenolysis of protolignin (X), Isolation of new dimer and trimer
Kenichi Sudo, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: Yezo spruce, *Picea jezoensis*, TLC, ^{1}H-NMR, UV spectroscopy

1972-005
広葉樹リグニンの加水分解物から新リグナン型化合物およびシリンギルグリセロール-β-シリンギルグリセロールエーテルの単離
大森茂俊、榊原　彰
北海道大学農学部
Isolation of a new lignan-type compound and syringylglycerol-β-syringyl ether from hydrolysis products of hardwood lignin
Shigetoshi Omori, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: *Fraxinus excelsissima*, ^{1}H-NMR, UV spectroscopy, IR spectroscopy, mass spectrometry

1972-006
ジオキサン-水によるリグニンの加水分解・スチルベン分解物について
佐野嘉拓、榊原　彰
北海道大学農学部
Hydrolysis of lignin with dioxane-water. On the stilbene type degradation products

Yoshihiro Sano, Akira Sakakibara,
Faculty of Agriculture, Hokkaido University
Keywords: Yezo spruce, *Picea jezoensis*, MWL, ^{1}H-NMR, UV spectroscopy, IR spectroscopy

1972-007
液安中金属ナトリウムによるリグニンの分解−III
山口　彰
林業試験場
Degradation of lignin by metallic sodium in liquid ammonia (III)
Akira Yamaguchi
Government Forest Experiment Station
Keywords: Yezo spruce, *Picea jezoensis*, guaiacyl-1,3-propanediol, ^{1}H-NMR,

1972-008
リグニンの分子運動におよぼす置換基の影響に関する研究
畠山兵衛
製品科学研究所
Effect of substituent group on molecular motion of lignin molecule
Hyoe Hatakeyama
Industrial Products Research Institute
Keywords: dioxane lignin, thiolignin, polystyrene, GPC

1972-009
塩素化リグニンの光化学反応による脱ハロゲン
島田謹爾[*1]、稲田　治[*2]
[*1] 林業試験場, [*2] 東京農工大学農学部
Dehalogenation of chlorolignin by photochemical reaction
Kinji Shimada[*1], Osamu Inada[*2]
[*1] Government Forest Experiment Station, [*2] Faculty of Agriculture, Tokyo University of Agriculture and Technology
Keywords: *Pinus densiflora, Fagus crenata,* MWL, irradiation of UV light, GLC

1972-010
過酢酸酸化のさいの β−アリルエーテル型構造の挙動
坂井克己、近藤民雄
九州大学農学部
Behavior of *β*-aryl ether type structure in peracetic acid oxidation
Kokki Sakai, Tamio Kondo
Faculty of Agriculture, Kyushu University
Keywords: *Pinus densiflora, Betula Tauschii*, MWL, acidolysis,

1972-011
特別講演、リグニン化学の進歩と今後の進路
榊原　彰
北海道大学農学部
Invited lecture: Progress and future prospects of lignin chemistry
Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: occurrence, distribution, formation, lignin in reaction wood, carbohydrates, structural model

1972-012
亜硫酸パルプ排液よりキシロースの単離
加藤孝二郎, 工藤正邦, 岡部次郎
山陽国策パルプ

Isolation of xylose from sulfite spent liquor
Koujiro Kato, Masakuni Kudo, Jiro Okabe
Sanyo Kokusaku Pulp Co., Ltd.
Keywords: sugar composition, pentose, hexose, extraction solvent

1972-013
リグニン中のキノイド構造
飯山賢治、中野準三
東京大学農学部
Quinoid structure in lignin
Kenji Iiyama, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: *Picea jezoensis*, MWL, thiolignin, lignosulfonic acid, visible light absorption spectrometry, *o*-quinone,

1972-014
高歩留パルプの酸化および還元漂白中におけるキノン類の挙動に関する研究
細谷修二、清家孝一、中野準三
東京大学農学部
Behavior of quinones during oxidative and reductive bleaching of high yield pulp
Shuji Hosoya, Koichi Seike, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: methoxy-*p*-quinone, 2,6-dimethoxy-p-quinone, 2-6-dimethoxybibenzoquinone, hydrogen peroxide

1972-015
パルプ廃液の色に関する研究（第 4 報）オキシリグニンと金属塩（2）
鮫島一彦、住本昌之、近藤民雄
九州大学農学部
Studies on the color of pulp waste liquor, IV. Oxylignin and metal salt (II)
Kazuhiko Sameshima, Masashi Sumimoto, Tamio Kondo
Faculty of Agriculture, Kyushu University
Keywords: aluminum ion, calcium ion, pH, gel filtration, lignin aluminum cpmplex

1972-016
パルプ製造排水の凝集処理に関する研究
徐道太郎、飯塚堯介、中野準三
東京大学農学部
Studies on coagulation treatment of waste liquor from pulp mill
Michitaro Jyo, Gyosuke Meshitsuka, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: *Pinus densiflora*, sulfite pulping, chlorine treatment, ferric sulfate, aluminum sulfate, pH

1972-017
ソーダ、酸素蒸解におけるリグニンの挙動について
十河村男、幡　克美
香川大学農学部
Behavior of lignin during soda-oxygen cooking
Murao Sogo, Katsumi Hata
Faculty of Agriculture, Kagawa University
Keywords: *Pinus densiflora*, *Fagus crenata*, MWL, UV absorption spectroscopy, IR absorption spectroscopy

1972-018
アミノベンゼンスルホン酸塩リグニンについて（II）

黒田健一、坂井克己、近藤民雄
九州大学農学部

On aminobenzenesulfonate lignin (II)

Ken-ichi Kuroda, Kokki Sakai, Tamio Kondo
Faculty of Agriculture, Kyushu University

Keywords: *Fagus crenata*, dioxane lignin, UV absorption spectroscopy, IR absorption spectroscopy

1972-019

高歩留り蒸煮木材のリファイニングにおいて剥離される中間層について

岩見田 紀[*1], 中野準三[*2]
[*1] 山陽国策パルプ, [*2] 東大農

Properties of middle lamella peeling during refining of steamed wood in sulfite semichemiical process

Tadashi Iwamida[*1], Junzo Nakano[*2]
[*1]Sanyo Kokusaku Pulp Co., Ltd., [*2] Faculty of Agriculture, the University of Tokyo

Keywords: *Picea jezoensis*, sulfite cooking, cell wall layers, electron microscope

1972-020

特別講演: Tappi Chromophores セミナーおよび酸素–アルカリ蒸解・漂白セミナーに参加して

中野準三
東京大学農学部

Invited lecture: Reports as an attendant at the Tappi Chromophore Seminar and Oxygen-Alkali Cooking, Bleaching Seminar

Junzo Nakano
Faculty of Agriculture, the University of Tokyo

第18回（1973.11.3-4）九州大学農学部

1973-A01
シナップ酸の還元および針葉樹におけるシリンギルリグニンの生成
中村吉紀、樋口隆昌
京都大学木材研究所
Reduction of sinapic acid and formation of syringyl lignin in conifer
Yoshiki Nakamura, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keyword: poplar, *Populus* spp., cherry, *Prunus densiflora*, red pine, *Pinus densiflora*, *Ginkgo biloba*, acidolysis, GC-MS analysis

1973-A02
p-クマリルアルコールの脱水素重合（II）. Coumaran の Configuration
中坪文明、樋口隆昌
京都大学木材研究所
Dehydrogenative polymerization of *p*-coumaryl alcohol (II), Configuration of coumaran substructures
Fumiaki Nakatsubo, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywordsynthesis of coumarans, ^{1}H-NMR

1973-A03
P-ヒドロキシシンナミルアルコール類の酵素的脱水素反応によるアリルグリセロールの生成
樋口隆昌、中坪文明、池田良久
京都大学木材研究所
Formation of arylglycerol by enzymatic dehydrogenation of *p*-hydroxycinnamyl alcohols
Takayoshi Higuchi, Fumiaki Nakatsubo, Yoshihisa Ikeda
Wood Research Institute, Kyoto University
Keywords: synthesis of arylglycerols, ^{1}H-NMR, laccase, peroxidase

1973-A04
プロトリグニンの水素化分解に関する研究（第12報）—炭素・炭素結合を有する二，三の2量体、3量体の単離、同定について
須藤賢一、榊原　彰
北海道大学農学部
Hydrogenolysis of protolignin (XII), Isolation and identification of some dimmers and trimers having carbon-carbon bond
Kenichi Sudo, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: *Picea jezoensis,* UV absorption spectrometry, ^{1}H-NMR, gas chromatography-mass spectrometry

1973-A05
磨砕木粉の酵素分解（1）
佐野嘉拓、榊原　彰
北海道大学農学部
Enzymatic degradation of milled wood (I)
Yoshihiro Sano, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: hemicellulase, cellulase, nitrobenzene oxidation

1973-A06
竹 MWL アシドリシス残渣のオゾン分解
棚橋光彦、中坪文明、樋口隆昌
京都大学木材研究所

Ozonolysis of acidolysis residue of bamboo MWL
Mitsuhiko Tanahashi, Fumiaki Nakatsubo, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: ^{1}H-NMR, synthesis of phenyl coumarone compound, UV absorption spectrometry

1973-A07
ヤチダモ材の加水分解物よりリグナン型化合物の単離
大森茂俊[*1]、榊原　彰[*2]
[*1]岩手大学農学部、[*2]北海道大学農学部
Isolation of lignan type compounds from hyrolysis products of *Fraxinus excelsissima*
Shigetoshi Omori[*1], Akira Sakakibara[*2]
[*1]Faculty of Agriculture, Iwate University, [*2]Faculty of Agriculture, Hokkaido University
Keywords: ^{1}H-NMR, column chromatography, mass spectrometry, UV absorption spectrometry, IR absorption spectrometry, ^{1}H-NMR

1973-A08
Björkman LCC の分別
越島哲夫、夜久富美子、田中龍太郎
大阪工業試験所
Fractionation of Björkman LCC
Tetsuo Koshijima, Fumiko Yaku, Ryutaro Tanaka
Government Industrial Research Institute, Osaka
Keywords: gel filtration, paper electrophoresis, molecular weight

1973-A09
リグニンの抗腫瘍作用
村上浩紀
九州大学農学部
Antitumor activity of lignin
Hiroki Murakami
Faculty of Agriculture, Kyushu University
Keywords: *Sasa veitchii*, *Pinus densiflora*, calcium lignosulfonate, mouse

1973-A10
南洋材リグニンの特性について(3) —*Eucalyptus Calophylla* の KINO 成分—
荻山紘一、安江保民
山形大学農学部
Characteristics of the tropical wood lignins (III), Kino of *Eucalyptus calophylla*
Koichi Ogiyama, Moritami Yasue
Faculty of Agriculture, Yamagata University
Keywords: anthocyanidine, leucoanthocyanidine, polymer

1973-A11
広巾 NMR によるリグニンの分子運動に及ぼす置換基の影響についての研究
村越　康、畠山兵衛
製品科学研究所
Studies on the effect of substituent on molecular motion of lignin by broad band NMR
Yasushi Murakoshi, Hyoe Hatakeyama
Industrial Products Research Institute
Keywords: polystyrene, model polymer, substituted styrene

1973-A12
アセトグアヤコン、イソオイゲノールおよび関連アリールエーテル類の光分解
佐分義正、善本知孝、南　享二

東京大学農学部
Photodegradation of acetoguaiacone, isoeugenol and related arylethers
Yoshimasa Saburi, Tomotaka Yoshimoto, Kyoji Minami
Faculty of Agriculture, the University of Tokyo
Keywords: lignin model compounds, gas liquid chromatography,

1973-A13
放射性同位元素標識リグニンの反応　—リグニンを構成する各炭素の KP 蒸解中の挙動
寺島典二、荒木　広、菅沼伸夫、神田　孝
名古屋大学農学部
Radiotracer experiments on lignin reactions, — Behavior of lignin carbons during kraft cooking process
Noritsugu Terashima , Hiroshi Araki, Nobuo Suganuma, Takashi Kanda
Faculty of Agriculture, Nagoya University
Keywords: *Pinus Thunbergii*, radiotracer, carbon 14, gel filtration

1973-A14
放射性同位元素標識リグニンの反応 —KP 蒸解中のリグニンと炭水化物との反応—
寺島典二、菅沼伸夫、荒木　広、神田　孝
名古屋大学農学部
Radiotracer experiments on lignin reactions, — Reaction of lignin with carbohydrates during kraft cooking process
Noritsugu Terashima , Nobuo Suganuma, Hiroshi Araki, Takashi Kanda
Faculty of Agriculture, Nagoya University
Keywords: *Pinus Thunbergii*, carbon 14, gel filtration, MWL, DHP, guaiacylglycerol-β-guaiacyl ether

1973-A15
リグニン及びフェノール類の着色
林　晄、木下恭介、中村卓司
立命館大学理工学部
Coloring of lignin and phenols
Akira Hayashi, Kyosuke Kinoshita, Takuji Nakamura
Faculty of Science and Engineering, Ritsumeikan University
Keywords: quinone polymer, ferric chloride, thiolignin, polarography

1973-A16
過酸化水素漂白における高歩留パルプ中のリグニンの反応に関する研究　—リグニン中間位モデル物質の反応—
細谷修二、中野準三
東京大学農学部
Reaction of lignin during bleaching of high yield pulp by hydrogen peroxide, — Reaction of intermediate lignin model compounds
Shuji Hosaya, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: model compounds, Mass spectrometry, GC-Mass, TLC, NMR spectroscopy

1973-A17
Guaiacylglycerol-β-guaiacyl ether の過酢酸酸化
沖　妙、大久保　克美、石川　久雄
愛媛大学農学部
Peracetic acid oxidation of guaiacylglycerol-β-guaiacyl ether
Tae Oki, Katsumi Okubo, Hisao Ishikawa,
Faculty of Agriculture, Ehime University
Keywords: lignin model compounds, vapor-phase oxidation, liquid phase oxidation

1973-A18
分子量分別したリグニンスルホン酸の電解酸化について
小川博嗣
東京工業試験所
Electrolytic oxidation of lignosulfonic acids fractionated by molecular weight
Hirotsugu Ogawa
Government Chemical Industrial Research Institute, Tokyo
Keywords: oxidation potential, pH

1973-A19
リグニンのオゾン処理　—溶媒の影響—
田中　治郎
林業試験場
Ozone treatment of lignin. –Effect of solvent
Jiro Tanaka
Government Forest Experiment Station
Keywords: larch, *Larix Kaempferi*, red pine, *Pinus densiflora,* wettability test

1973-B01
過酢酸気相漂白とその特色について
大久保克美、沖　妙、石川久雄
愛媛大学農学部
Vapor phase bleaching by peracetic acid, and its special feature
Katsumi Okubo, Tae Oki, Hisao Ishikawa
Faculty of Agriculture, Ehime University
Keywords: Douglas fir, *Pseudotsuga taxifolia*, UKP, dioxane lignin

1973-B02
各種ベースによるホロパルプ製造
松浦洋
日本紙パルプ研究所
Holopulping process using different bases
Hiroshi Matsuura
Japan Pulp and Paper Research Institute, Inc.
Keywords: holopulp, holocellulose, chlorine dioxide, recovery process, Na-base holopulp, Mg-base holopulp

1973-B03 中止

1973-B04
酸素・アルカリ処理によるアカマツ MWL の分解
十河　村男、幡　克美
香川大学農学部
Degradation of MWL of Japanese red pine by oxygen-alkali treatment
Murao Sogo, Katsumi Hata
Faculty of Agriculture, Kagawa University
Keywords: *Pinus densiflora,* MWL, UV spectroscopy, gel filtration

1973-B05
針葉樹クラフトパルプの酸素漂白
永野正，石井彰一，宮尾再青，松井泰彦
東洋パルプ株式会社
Oxygen bleaching of softwood kraft pulp
Tadashi Nagano, Shoichi Ishi, Saisei Miyao, Yasuhiko Matsui

Toyo Pulp Co., Ltd
Keywords: COD, cooking spent liquor, green liquor, kappa number

1973-B06
酸素漂白について
田渕博，川島功，山田洋三
紀州製紙株式会社
On the oxygen bleaching
Horoshi Tabuchi, Isao Kawashima, Yozo Yamada
Kishu Paper Co., Ltd.
Keywords: heavy metal ion, cellulose protecting agents, brightness stability

1973-B07
パルプ工業の無公害化へのアプローチ
御田昭雄^{*1}、平井久雄^{*2}
^{*1} 東京工業試験所、^{*2} チッソエンジニアリング株式会社
Approaches to pollution free pulp industry
Akio Mita^{*1}, Hisao Hirai^{*2}
^{*1}Government Chemical Industrial Research Institute, Tokyo, ^{*2}Chisso Engineering Co.Ltd.
Keywords: closed system, unit process,

1973-B08
SO_2＋$MgSO_4$　蒸解廃液からの薬品の回収と活性炭の製造について
林　治助^{*1}，戸坂圀夫^{*1}、伴内正樹^{*2}
^{*1} 北海道大学工学部、^{*2} プロセス資材株式会社
Recovery of chemicals and production of activated carbon from waste liquor of pulping with SO_2 + $MgSO_4$
Jisuke Hayashi^{*1}, Kunio Tosaka^{*1}, Masaki Bannai^{*2}
^{*1}Faculty of Engineering, Hokkaido University, ^{*2}Process Shizai Co. Ltd.
Keywords: white birch, *Betula Tauschii,*

1973-B09
γ線照射によるパルプ製造廃水の淡色化に関する研究
飯塚堯介、中野準三
東京大学農学部
Reduction of color intensity of pulp mill effluent liquor byγ-ray irradiation
Gyosuke Meshitsuka, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: thiolignin, lignosulfonic acid, cobalt 60, peroxide radical

1973-B10
亜硫酸系パルプ廃液中の有機物成分の分取
猪狩俶将、横山正一郎
東京工業試験所
Separation of organic components from sulfite pulp waste liquor
Yoshimasa Ikari, Shoichiro Yokoyama
Government Chemical Industrial Research Institute, Tokyo
Keywords: Yezo spruce, *Picea jezoensis, Abies Mayriana*, NSCP, BOD,

1973-B11
パルプ製造廃水の凝集処理に関する研究　—凝集機構について—
徐道太郎、飯塚堯介、中野準三
東京大学農学部
Studies on the coagulation treatment of pulp mill effluent liquor. –Mechanism of coagulation
Jyo Michitaro, Gyosuke Meshitsuka, Junzo Nakano.

Faculty of Agriculture, the University of Tokyo
Keywords: lignosulfonate, thiolignin, sulfomethyl thiolignin, zeta potential, electrokinetic potential, aluminum ion

1973-B12
クラフトパルプ廃水のオゾン併用活性汚泥処理 —処理効率と諸パラメーターについて—
上嶋　洋、赤松　勲
四国工業技術試験所
Treatment of kraft pulp mill effluent by activated sludge combined with ozone treatment. -Efficiency and parameters of the treatment
Hiroshi Kamishima, Isao Akamatsu
Government Industrial Research Institute, Shikoku
Keywords: BOD, COD(Mn),

1973-B13
製紙スラッジを原料とする吸着剤の製造研究 —各種スラッジの示差熱分析結果と製造条件について—
前松陸郎、曽我部隆紀、芳地全保、谷　静男
愛媛県製紙試験所
Production of adsorbent from pulp mill sludge. –Differential thermal analyses of various sludge and conditions of preparation
Mutsuo Maematsu, Takanori Sogabe, Masayasu Hochi, Shizuo Tani
Pulp and Paper Research Institute of Ehime Prefecture.
Keywords: recycled paper sludge, straw pulp sludge,

1973-B14
クラフトパルプ廃水の石灰処理（V）—廃水中のリグニンの分子量分布の石灰処理に及ばす影響—
加藤俊作、久保隆昌、木村　裕
四国工業技術試験所
Treatment of kraft pulp mill effluent with lime (V), Effect of molecular weight distribution of lignin in the effluent on lime treatment
Shunsaku Kato, Takamasa Kubo, Yutaka Kimura
Government Industrial Research Institute, Shikoku
Keywords: COD, TOC, gel filtration,

1973-B15
BKP 製造における工程別排水の性状およびその凝集沈澱処理
上埜武夫，守屋正夫，竹下　登
山陽国策パルプ株式会社
Properties and sedimentation treatment of effluents from kraft pulping and bleaching processes
Takeo Ueno, Masao Moriya, Noboru Takeshita
Sanyo Kokusaku Pulp Co., Ltd.
Keywords: *Pseudotsuga taxifolia*, COD, chromaticity, lignin, sugar, color analysis

1973-B16
パルプ廃水処理
白川精一，木村勇，川添早苗，荒牧幹男
三菱重工業株式会社
Pulp effluents treatment
Seiichi Shirakawa, Isamu Kimura, Sanae Kawazoe, Mikio Aramaki
Mitsubishi Heavy Industries, Ltd.
Keywords: sedimentation, KP, SP, SCP, fermentation spent liquor, flocculant, colloid titration

第19回（1974.10.19-20）秋田大学教育学部

1974-101
ヤドリギ（*Viscum album*）のリグニンとO－メチル基転位酵素
黒田宏之、樋口隆昌
京都大学木材研究所
Lignin in *Viscum album*, and *O*-methyl transferase
Hiroyuki Kuroda, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: ferulic acid, sinapic acid, OMT inhibitor

1974-102
シラカンバ新生組織へのフェニールアラニン-^{14}C（U）の取り込みとリグニン形成
三宅基夫、寺沢　実、奥山　寛
帯広畜産大学
Incorporation of phenylalanine-^{14}C(U) into newly formed xylem tissue of Betula Tauschii *and lignin formation*
Motoo Miyake, Minoru Terasawa, Hiroshi Okuyama
Obihiro University of Agriculture and Veterinary Medicine
Keywords: platyophylloside, platyphylldioloside, betuloside

1974-103
ポプラリグニンのパラハイドロオキシ安息香酸の生合成
寺島典二、岡田基光、神田　孝
名古屋大学農学部
Biosynthesis of *p*-hydroxybenzoic acid in poplar lignin
Noritsugu Terashima, Motomitsu Okada, Takashi Kanda
Faculty of Agriculture, Nagoya University
Keywords: *Populus nigra* X Populus *Maximowiczii*, ^{14}C-labeled precursor

1974-104
Non-Woody リグニンについて　—ナシの石細胞とモモの内果皮リグニン—
黒田宏之、近藤民雄
九州大学農学部
On the non-woody lignin. –Lignins in stone cell of pear (*Pyrus pyrifolia var. culta*) and in endocarp of peach (*Amygdalus persica*)
Hiroyuki Kuroda, Tamio Kondo
Faculty of Agriculture, Kyushu University
Keywords: dioxane lignin, nitrobenzene oxidation, ethanolysis

1974-105
圧縮アテ材リグニンの化学構造について
安田征市、榊原　彰
北海道大学農学部
Chemical structure of lignin in compression wood
Seichi Yasuda, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: *Larix leptolepis, p*-hydroxyphenyl nucleus, guaiacyl nucleus, MWL，NMR

1974-106
カラマツアルカリリグニンの GPC について
香川詔士、長谷川修
関東学院大学工学部
On gel permeation chromatography of alkali lignin from larch
Shoji Kagawa, Osamu Hasegawa

Kanto Gakuin University
Keywords: *Larix leptolepis,* molecular weight distribution, air oxidation of alkali lignin, IR spectrum

1974-107
プロトリグニンの水素化分解に関する研究（第 13 報）—2，3 量体の単離、同定について—
須藤賢一、榊原　彰
北海道大学農学部
Hydrgenolysis of protolignin (XIII), –Isolation and identification of dimers and trimers
Kenichi Sudo, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: Yezo spruce, *Picea jezoensis,* α-conidendrin, matairesinol

1974-108
液安中金属ナトリウムによるリグニンの分解　—G 核及び P 核を有する二量体の単離—
山口　彰
林業試験場
Degradation of lignin by metallic sodium in liquid ammonia, — Isolation of dimer containing G and P units—
Akira Yamaguchi
Government Forest Experiment Station
Keywoeds: Yezo spruce, *Picea jezoensis,* ^{1}H-NMR, mass spectrometry

1974-109
竹リグニンのアシドリシス残渣のオゾン分解
棚橋光彦、中坪文明、樋口隆昌
京都大学木材研究所
Ozonolysis of acidolysis residue of bamboo lignin
Mitsuhiko Tanahashi, Fumiaki Nakatsubo, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: lignin model compound,

1974-110
ジオキサン—水によるリグニンの加水分解
佐野嘉拓、榊原　彰
北海道大学農学部
Hydrolysis of lignin with dioxane-water
Yoshihiro Sano, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: synthesis of compounds related hydrolysis products, gel chromatography

1974-111
リグニンの加溶媒分解 (第3報) –トレーサー法による反応の検討–
可知省吾[*1]，荒木廣[*2]，寺島典二[*2]
日本紙パルプ研究所[*1]，名古屋大学農学部[*2]
Solvolysis of lignin (III), Examination of reaction by the radioisotope tracer techniques
Shogo Kachi[*1], Hiroshi Araki[*2], Noritsugu Terashima [*2]
[*1]Japan Pulp and Paper Research Institute, Inc, [*2] Faculty of Agriculture、 Nagoya University
Keywords: MWL, radioisotope, carbon-14, tritium

1974-112
1,2-Diarylpropane-1,3-diols の合成
中坪文明、樋口隆昌
京都大学木材研究所
Synthesis of 1,2-diarylpropane-1,3-diols
Fumiaki Nakatsubo, Takayoshi Higuchi

Wood Research Institute, Kyoto University
Keywords: ^{1}H-NMR, configuration, preparative TLC

1974-113
グアヤシルグリセロール-β-グアヤシルエーテルの合成
細谷修二、中野準三
東京大学農学部
Synthesis of guaiacylglycerol-β–guaiacyl ether
Shuji Hosoya, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: ^{1}H-NMR, mass spectrometry

1974-114
Guaiacylglycerol-β-guaiacylether の酸素アルカリ分解
沖 妙、大久保克美、石川久雄
愛媛大学農学部
Degradation of guaiacylglycerol-β-guaiacylether by oxygen-alkali
Tae Oki, Katsumi Okubo, Hisao Ishikawa
Faculty of Agriculture, Ehime University
Keywords: peracetic acid oxidation, thin layer chromatography, gas chromatography

1974-115
リグニン分子運動のモデルポリマーによる考察
畠山兵衛[*1]、木村 実[*2]
[*1] 製品科学研究所, [*2] 東京大学農学部
Simulation of molecular motion of lignin using a model polymer
Hyoe Hatakeyama[*1], Minoru Kimura[*2]
[*1]National Institute of Advanced Industrial Science and Technology, [*2]Faculty of Agriculture, the University of Tokyo
Keywords: TBA, torsion brade analysis, DSC, broad band NMR,

1974-116
特別講演、Past and Present Challenges in Lignin Chemistry
Conrad Schuerch
ニューヨーク州立大、米、シラキウス
Invited lecture: Past and Present Challenges of Lignin Chemistry
Conrad Schuerch
New York State University, Syracuse. USA
Keywords: Klason, Staudinger, Freudenberg, Hibbert, Erdtman, heterogeneity, macromolecule, molecular weight, cellulose, UV spectroscopy, IR spectroscopy, protolignin, milled wood lignin,
biphenyl structure, phenolic hydroxyl group content, ^{13}C-NMR, microscopy, pulping, bleaching

1974-201
酸素アルカリ蒸解におけるブナリグニンの挙動
十河村男、幡 克美
香川大学農学部
Behavior of beech lignin during oxygen-alkali cooking
Murao Sogo, Katsumi Hata
Faculty of Agriculture, Kagawa University
Keywords: *Fagus crenata*, MWL, UV spectroscopy, gaschromatography

1974-202
酸素アルカリ蒸解におけるリグニンの挙動
青柳哲夫、細谷修二、中野準三

東京大学農学部
Behavior of lignin during oxygen-alkali cooking
Tetsuo Aoyagi, Syuji Hosoya, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: apocinol, acetovanillon, gas chromatography, quinone, radical

1974-203
アルカリ酸素漂白におけるプロテクターの保護機構
林　治助[*1]、山田紹良[*1]、戸坂圀夫[*1]、小泉正弘[*2]
[*1] 北海道大学工学部, [*2] 東洋パルプ株式会社
Mechanism of protection of cellulose degradation by protectors in oxygen-alkali bleaching
Jisuke Hayashi[*1], Akira Yamada[*1], Kunio Tosaka[*1], Masahiro Koizumi[*2]
[*1] Faculty of Engineering, Hokkaido University, [*2]Toyo Pulp Co. Ltd.
Keywords: magnesium carbonate, glucose, xylose, reducing monosaccharide, water soluble lignin

1974-204
クラフトパルプのオゾン漂白　—針葉樹と広葉樹パルプの漂白性について
上嶋　洋、藤井利郎、赤松　勲
四国工業技術試験所
Ozone bleaching of kraft pulp. –Bleachability of softwood pulp and hardwood pulp
Hiroshi Kamishima, Toshiro Fujii, Isao Akamatsu
Government Industrial Research Institute, Shikoku
Keywords: Japanese red pine, *Pinus densiflora*, beech, *Fagus crenata*,

1974-205
酸素アルカリ処理に関する研究（V）—酸素漂白シーケンスについて（2）—
西田友昭、坂井克己、近藤民堆
九州大学農学部
Studies on oxygen-alkali treatment (V), —Peracetic acid bleaching of kraft pulp prebleached by oxygen-alkali (2)—
Tomoaki Nishida, Kokki Sakai, Tamio Kondo
Faculty of Agriculture, Kyushu University
Keywords: white birch, *Betula Tauschii*, analysis of variance, brightness

1974-206
高収率パルプに関する研究
御田昭雄[*1]、山本登久男[*2]、勝地光雄[*2]、勝山敦弘[*2]、平井久夫[*3]、赤羽利昭[*3]
[*1] 東京工業試験所、[*2] 静岡県製紙工業試験所、[*3] チッソエンジニアリング
Studies on the high yield pulp
Akio Mita[*1], Tokuo Yamamoto[*2], Mitsuo Katsuji[*2], Atsuhiro Katsuyama [*2], Hisao Hirai[*3], Toshiaki Akabane[*3]
[*1]Government Industrial Research Institute, Tokyo, [*2]Paper Research Institute of Shizuoka Prefecture, [*3]Chisso Engineering Co. Ltd.
Keywords: Douglas fir, *Pseudotsuga taxifolia*, lauan, *Shorea sp.*, straw, bagasse, SOX chemimechanical pulp,

1974-207
南洋材リグニンの特性について(4)—パルプ排液の着色に及ぼす高分子ロイコアントシアニジンの影響—
荻山紘一、安江保民
山形大学農学部
Characteristics of the tropical wood lignins. IV. –Effect of high molecular leuco-anthocyanidins on coloring of pulp waste liquor
Koichi Ogiyama, Moritami Yasue
Faculty of Agriculture, Yamagata University
Keywords: *Eucalyptus calophylla*, UV spectroscopy, benzoquinone

1974-208
SCP 廃液について（4）—廃液中の Xylan—
稲田　治、鮫島一彦、近藤民雄
九州大学農学部
On the waste liquor of SCP (IV), –Xylan in waste liquor
Osamu Inada, Kazuhiko Sameshima, Tamio Kondo
Faculty of Agriculture, Kyushu University
Keywords: *Carpinus* sp. white birch, *Betula Tauschii*, beech, *Fagus crenata*, kapur, *Doryobalanops*, white lauan, *Pentacme* sp.

1974-209
石巻地先における底質汚染の調査結果について
上柿明子、渡辺丈夫、佐藤春雄、曾根　光
宮城県公害技術センター
Report of sediment contamination survey at onshore of Ishinomaki
Akiko Kamigaki, Takeo Watanabe, Haruo Sato, Hikaru Sone
Pollution Reserch Center of Miyagi Prefecture
Keywords: pulp effluent, COD, TOC, sulfide

1974-210
秋田湾海域汚染とスス水発生について
加藤治男
秋田県水産試験場
Sea water pollution and cause of sooty water at Akita bay
Haruo Kato
Akita Fisheries Experiment station
Keywords: COD, SS, suspended substance,

1974-211 中止

1974-212
BKP 製造工程から発生する各種漂白排水の性状及びその排水処理
竹下　登，上埜武夫，守屋正夫
山陽国策パルプ株式会社
Properties and treatment of effluents from kraft pulp bleaching processes
Noboru Takeshita, Takeo Ueno, Masao Moriya
Sanyo Kokusaku Pulp Co., Ltd.
Keywords: molecular weight distribution, sedimentation process, activated sludge process

1974-213
パルプ廃液の色に関する研究　—廃液処理時の色の挙動について—
鮫島一彦、石崎貞二、住本昌之、近藤民堆
九州大学農学部
Studies on the color of pulping waste liquor, –Behavior of coloring matter during treatment of waste liquor
Kazuhiko Sameshima, Teiji Ishizaki, Masashi Sumimoto, Tamio Kondo
Faculty of Agriculture, Kyushu University
Keywords:: activated carbon, dialysis, aluminum sulfate

1974-214
パルプ廃水の炭素質材料等による浄化
里中聖一
北海道大学農学部
Purification of pulp mill effluent with carbonaceous materials

Seichi Satonaka
Faculty of Agriculture, Hokkaido University
Keywords: activated carbon, KP, SP, NSC. bark, Japanese oak, *Quercus crispula*

1974-215
パルプ漂白排水中の塩素化リグニンの紫外線分解
島田謹爾
林業試験場
Degradation of chlorinated lignin in pulp bleach effluent by ultraviolet light
Kinji Shimada
Forestry and Forest Product Research Institute
Keywords: red pine, *Pinus densiflora*, KP, COD, gas chromatography

1974-216
γ 線照射によるパルプ製造排水の淡色化について
飯塚堯介、中野準三
東京大学農学部
Reduction of color intensity of pulp mill effluent by γ-ray irradiation
Gyosuke Meshitsuka, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: thiolignin, lignosulfonic acid, lignin model compounds, COD, active oxygen species, conjugated double bonds, air bubbling

第20回（1975.10.20-21）名古屋大学農学部

1975-101
バクテリアによるリグニンモデル化合物の分解(1)
森　義博、福住俊郎，南　享二
東京大学農学部
Degradation of lignin model compounds by bacteria (I)
Yoshihiro Mori, Toshiro Fukuzumi, Kyoji Minami
Faculty of Agriculture, the University of Tokyo
Keywords: *Pseudomonas putida, Pseudomonas fluorescens, Pseudomonas dacunhae, Pseudomonas ovalis, Pseudomonas surfactasimilas*, DHP,

1975-102
木材腐朽菌によるβ−エーテル化合物の分解
松本　久、福住俊郎，南　享二
東京大学農学部
Degradation of β-ether compounds by wood rotting fungi
Hisashi Matsumoto, Toshio Fukuzumi, Kyoji Minami
Faculty of Agriculture, the University of Tokyo
Keywords: *Perenniporia subacida, Irpex lacteus, Trametes sanquineus*

1975-103
リグニン関連合成高分子の生分解
林　英一[*1]、畠山兵衛[*2]、原口隆英[*1]
[*1] 東京農工大学農学部、[*2] 製品科学研究所
Biodegradation of synthetic polymer related to lignin
Eiichi Hayashi[*1],Hyoe Hatakeyama[*2], Takafusa Haraguchi[*1]
[*1]Faculty of Agriculture, Tokyo University of Agriculture and Technology, [*2] Industrial Products Research Institute
Keywords: poly-(*p*-hydroxy styrene), poly-(3-methoxy-4-hydroxy styrene), poly-(3,5-dimethoxy-4-hydroxy styrene), molecular weight distribution, UV spectrometry

1975-104
白色腐朽菌ヒラタケによるリグニンの分解
広居忠量[*1]，K.E. Eriksson[*2]
[*1] 林業試験場，[*2]STFI
Degradation of lignin by white rot fungus *Pleurotus ostreatus*
Tadakazu Hiroi[*1], K.E. Eriksson[*2]
[*1]Government Forest Experiment Station, [*2]Swedish Pulp and Paper Research Institute
Keywords: MWL, *Chamaecyparis obtuse*, kraft lignin, *Pinus densiflora,* Ca-lignosulfonate, molecular weight distribution

1975-105
ラッカーゼによりシリンガ酸から生成した*o*-キノン誘導体の構造について
石原達夫、石原光朗
林業試験場
Structure of *o*-quinone derivatives derived from syringic acid by laccase
Tatsuo Ishihara, Mitsuro Ishihara
Government Forest Experiment Station
Keywords: *Polyporus versicolor,* UV spectrometry, 2,6-dimethoxy-p-benzoquinone

1975-106
木材腐朽菌によるクラフト廃液の脱色
福住俊郎、西田篤實、島崎徹郎、南　享二

東京大学農学部
Decolorization of kraft pulp mill effluent by wood rotting fungi
Toshio Fukuzumi, Atsumi Nishida, Tetsuro Shimazaki, Kyoji Minami
Faculty of Agriculture, the University of Tokyo
Keywords: *Tinctoporia* sp., *Trametes* sp., *Tryromyces* sp., *Pleurotus* sp., *Pholiota* sp., *Phallinus* sp. UV spectrometry, gel filtration

1975-107
南洋材リグニンの特性(5)赤ラワン、ブナ材の着色
荻山紘一、安江保民
山形大学農学部
Characteristics of the tropical wood lignins (V), –Coloration of red lauan and beech wood
Koichi Ogiyama, Moritami Yasue
Faculty of Agriculture, Yamagata University
Keywords: *Shorea negrosensis*, *Fagus crenata*, reflectance spectrum,

1975-108
ジオキサン—水によるリグニンの加水分解 —モデル化合物の加水分解—
佐野嘉拓、榊原 彰
北海道大学農学部
Hydrolysis of lignin with dioxane-water, —Hydrolysis of model compounds—
Yoshihiro Sano, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: synthesis of model compounds, NMR, mass spectrometry, thin layer chromatography

1975-109
ジオキサン—水によるプロトリグニンの加水分解 —新 3 量体の単離—
大森茂俊[*1]、榊原 彰[*2]
[*1] 岩手大学農学部、[*2] 北海道大学農学部
Hydrolysis of protolignin with dioxane-water, –Isolation of a new trimer—
Shigetoshi Omori[*1], Akira Sakakibara[*2]
[*1]Faculty of Agriculture, Iwate University, [*2]Faculty of Agriculture, Hokkaido University
Keywords: *Fraxinus excelsissima*, IR spectroscopy, UV spectroscopy, Mass spectrometry, NMR

1975-110
広葉樹プロトリグニンの水素化分解 —2量体の単離と構造解析について
須藤賢一[*1]、岸 政美[*2]、榊原 彰[*2]
[*1] 林業試験場、[*2] 北海道大学農学部
Hydrogenolysis of hardwood protolignin, –Isolation and structural analysis of a dimer
Kenichi Sudo[*1], Masami Kishi[*2], Akira Sakakibara[*2]
[*1]Forestry and Forest Product Research Institute,[*2]Faculty of Agriculture, Hokkaido University
Keywords: *Fraxinus excelsissima*,TLC, Mass spectrometry, ^{1}H-NMR, dimethoxylariciresinol

1975-111
アテ材リグニンの水素化分解 —縮合型新2量体その他の単離
安田征市、榊原 彰
北海道大学農学部
Hydrogenolysis of lignin in compression wood. Isolation of a new condensed type dimmer and other compounds
Seiichi Yasuda, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: larch, *Larix Kaempferi*, TLC, Mass spectrometry, ^{1}H-NMR,

1975-112

リグニンの加溶媒分解（第５報）−トレーサー法による反応の検討（3)−
可知省吾[*1]，荒木廣[*2]，寺島典二[*2]，神田孝[*2]
[*1] 日本紙パルプ研究所，[*2] 名古屋大学農学部
Solvolysis of lignin (V), −Comparison of solvolysis lignins with other lignins by the radioisotope tracer techniques (3) −
Shogo Kachi[*1], Hiroshi Araki[*2] , Noritsugu Terashima [*2], Takashi Kanda [*2]
[*1]Japan Pulp and Paper Research Institute, Inc, [*2] Faculty of Agriculture, Nagoya University, **Keywords**: solvolysis, lignin, radioisotope, carbon-14, tracer

1975-113
Björkman LCC 中のリグニンに結合する糖の結合様式
越島哲夫、夜久富美子、田中龍太郎
大阪工業技術試験所
Linkage type of sugar unit bound to lignin in Björkman LCC
Tetsuo Koshijima, Kumiko Yaku, Ryutaro Tanaka
Government Industrial Research Institute, Osaka
Keywords: DEAE Sephadex column chromatography, electrophoresis,

1975-114
シラカンバ樹皮のリグニン
三宅基夫、寺沢 実、奥山 寛
帯広畜産大学
Lignin in the bark of birch
Motoo Miyake, Minoru Terasawa, Hiroshi Okuyama
Obihiro University of Agriculture and Veterinary Medicine
Keywords: *Betula Tauschii*, cork tissue, nitrobenzene oxidation, suberin, pectin

1975-115
3,5−2 置換 *p*-ヒドロキシケイヒアルコールの脱水素重合
棚橋光彦、武内英夫、樋口隆昌
京都大学木材研究所
Dehydrogenative polymerization of 3,5-disubstituted *p*-hydroxycinnamyl alcohol
Mitsuhiko Tanahashi, Hideo Takeuchi, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: 5-iodo-coniferyl alcohol, 3,5-diiodo-*p*-coumaryl alcohol, sinapyl alcohol, ^{1}H-NMR

1975-116
ヤドリギリグニンの生合成
黒田宏之、樋口隆昌
京都大学木材研究所
Biosynthesis of lignin in *Viscum album*
Hiroyuki Kuroda, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: *O*-methyl transferase, OMT, guaiacyl lignin, syringyl lignin, *Celtis sinensis*, MWL, ^{13}C-NMR, radio tracer, phenylalanine-U-^{14}C

1975-117
傷害，病害に伴うサツマイモ、ウリ類におけるリグニン形成
瓜谷郁三、寺島典二、小島峯雄
名古屋大学農学部
Lignin formation in sweet potato and cucumber caused by injury or blight
Ikuzo Uritani, Noritsugu Terashima, Mineo Kojima
Faculty of Agriculture, Nagoya University
Keywords: sweet potato, *Ipomea batatas*, cucumber, *Cucumis sativus*, lignification, injury, blight

1975-118
特別講演、植物病態組織でのリグニン生合成
浅田泰次、大口富三、松本勲
愛媛大学農学部
Invited lecture: Biosynthesis of lignin in diseased plant tissue
Yasuji Asada, Tomizo Ohguchi, Isao Matsumoto
Faculty of Agriculture, Ehime University
Keywords: *Alternaria japonica*, *Peronospora parasitica*, peroxidase, isoperoxidase, lignification inducer

1975-201
ユーカリ材黒液の高分子的性質
岡山隆之、大江礼三郎
東京農工大学農学部
Macromolecular properties of black liquor from eucalyptus wood
Takayuki Okayama, Reizaburo Ooe
Faculty of Agriculture, Tokyo University of Agriculture and Technology
Keywords: kraft lignin, polyphenol, *Eucalyptus marginata*, gel filtration, molecular weight

1975-202
Mg ベース SCP について（4）—廃液の燃焼性と薬品回収—
周　森、住本昌之、近藤民雄
九州大学農学部
On the Mg-base SCP. IV. –Combustibility of waste liquor and recovery of chemicals
Syu Sin, Masashi Sumimoto, Tamio Kondo
Faculty of Agriculture, Kyushu University
Keywords: magnesium oxide, heat of combustion, semichemical pulp

1975-203
無機吸着剤によるパルプ廃液の処理
猪狩椒将[*1]、横山正一郎[*1]、村上達夫[*2]
[*1] 東京工業試験所、[*2]富士化学工業株式会社
Treatment of pulp waste liquor with inorganic adsorbent
Yoshimasa Ikari[*1], Shoichiro Yokoyama[*1], Tatsuo Murakami[*2]
[*1]Government Industrial Research Institute, Tokyo, [*2]Fuji Chemical Co. Ltd.
Keywords: COD, BOD, TOC, gel filtration

1975-204
粘土懸濁液の粘性に与える高分子量リグニンスルホン酸の影響
小山　実
東京工業試験所
Effect of high molecular lignosulfonic acid on the viscosity of clay suspension
Minoru Koyama
Government Industrial Research Institute, Tokyo
Keywords: montmorillonite, kaolinite,

1975-205
リグニン中のフリーラジカルについて
飯塚堯介、中野準三
東京大学農学部
On the free radical in lignin
Gyosuke Meshitsuka, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: ESR spectrum, pH, EDTA, metal ion, reducing agents

1975-206
KP 蒸解における炭水化物からの色
鮫島一彦、高村憲男
高知大学農学部
Color originated from carbohydrate in kraft cooking
Kazuhiko Sameshima, Norio Takamura
Faculty of Agriculture, Kochi University
Keywords: *Betula Tauschii*, xylan, xylose, holocellulose, UV and Visible light spectroscopy

1975-207
クラフトパルプ漂白排水中の低分子化合物について
金沢健治、細谷修二、中野準三
東京大学農学部
Low molecular weight compounds in kraft pulp bleach effluent
Kenji Kanazawa, Shuji Hosoya, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: thiolignin, TLC, gas chromatography, mass spectrometry

1975-208
パルプ漂白廃液中の低分子有機成分について
島田謹爾
林業試験場
Low molecular organic compounds in pulp bleach effluent
Kinji Shimada
Government Forest Experiment Station
Keywords: Japanese red pine, *Pinus densiflora*, BKP, GC/MS,

1975-209
高収率パルプ白色度向上について—亜塩素酸塩利用の効果—
加納　直，岩見田糺，角　祐一郎
山陽国策パルプ株式会社
Peroxide bleaching of chemimechanical pulps, – Effect of pretreatment with sodium chlorite
Tadashi Kano, Tadashi Iwamida, Yuichiro Sumi
Sanyo Kokusaku Pulp Co., Ltd.
Keywords: chemimechanical pulp, peroxide bleaching, pretreatment, sodium chlorite, brightness

1975-210
パルプのオゾン漂白におけるセルロース保護剤の効果
上嶋　洋、藤井利郎、赤松　勲
四国工業技術試験所
Effect of cellulose protector in ozone bleaching of pulp
Hiroshi Kamishima, Toshio Fujii, Isao Akamatsu
Government Industrial Research Institute, Shikoku
Keywords: *Pseudotsuga taxifolia*, iron, copper, zinc, cobalt, manganese, organic protector

1975-211
酸素・アルカリ蒸解におけるリグニンの挙動について　—α−カルボニル基に基づく新しい反応サイト
青柳哲夫、細谷修二、中野準三
東京大学農学部
Behavior of lignin during oxygen-alkali cooking, -New reaction site based on a-carbonyl group
Tetsuo Aoyagi, Shuji Hosoya, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: lignin model compounds, reaction mechanism, benzyl alcohol, benzyl ether

1975-212
Guaiacylglycerol-β-guajacy1ether の酸素・アルカリ酸化分解
沖　妙、大久保克美、石川久雄
愛媛大学農学部
Oxygen-alkali degradation of guaiacy1glycerol-β–guajacy1ether
Tae Oki, Katsumi Okubo, Hisao Ishikawa
Faculty of Agriculture, Ehime University
Keywords: UV spectrometry, quinone, pH dependence

1975-213
亜硫酸ソーダ—酸素・アルカリ2段蒸解試験並びに蒸解時におけるリグニンの挙動について
林　忠和、幡　克美、十河村男、山崎　徹
香川大学農学部
Two stage sodium sulfite-oxygen alkali cooking test and behavior of lignin during the cooking
JongHer Lin, Katsumi Hata, Murao Sogo, Toru Yamasaki
Faculty of Agriculture, Kagawa University
Keywords: Japanese red pine, *Pinus densiflora*, beech, *Fagus crenata*, IR spectrometry

1975-214
酸素・アルカリ処理に関する研究　—廃液の濃縮過程で生ずる沈殿について—
浅野　勲、坂井克己、近藤民雄
九州大学農学部
Studies on the oxygen alkali treatment, –On the precipitant formed in the concentration process of waste liquor
Isao Asano, Kokki Sakai, Tamio Kondo
Faculty of Agriculture, Kyushu University
Keywords: birch, *Betula tauschii,* scaling problem,

1975-215
アルカリ，酸素漂白におけるプロテクターの保護機構（第３報）
山田紹良、小森重男、林　治助、戸坂圀夫
北海道大学工学部
Protection mechanism by protectors during alkali oxygen bleaching
Akira Yamada, Shigeo Komori, Jisuke Hayashi, Kunio Tosaka
Faculty of Engineering, Hokkaido University
Keywords: softwood UKP, hydroxyl radical, reducing sugar, glucose

1975-216
アルカリ-酸素蒸解に関する研究（第 3 報）ふりかけ法による稲わらからのパルプ製造について
戸坂圀夫[*1]、渡辺貞良[*1]、林　治助[*1]、山田邦重[*2]、小川文人[*3]
[*1] 北海道大学工学部、[*2] 株式会社ほくさん、[*3] 王子製紙株式会社
Studies on the oxygen alkali cooking (III), Pulp production from rice straw by sprinkling process
Kunio Tosaka [*1], Sadayoshi Watanabe[*1], Jisuke Hayashi[*1],Kunishige Yamada[*2], Fumito Ogawa[*3]
[*1]Faculty of Engineering, Hokkaido University, [*2]Hokusan Co. Ltd., [*3]Oji Paper Co. Ltd
Keywords: tensile strength, burst factor, breaking length,

1975-217
非木材パルプに関する研究
御田昭雄[*1]、山本登久男[*2]、勝地光雄[*2]、山崎恒夫[*2]、勝山敦弘[*2]、
赤羽利昭[*3]、梅木一義[*3]
[*1] 東京工業試験所、[*2] 静岡県製紙工業試験所、[*3] チッソエンジニアリング株式会社
Studies on non-woody pulp
Akio Mita[*1], Tokuo Yamamoto[*2], Mitsuo Katsuji[*2], Tsuneo Yamazaki[*2], Atsuhiro Katsuyama[*2], Toshiaki

Akabane[*3], Kazuyoshi Umeki[*3]
[*1]Government Industrial Research Institute, Tokyo, [2]Paper Research Institute of Shizuoka Prefecture, [*3]Chisso Engineering Co. Ltd.

Keywords: straw, bagasse, silica, SOX chemimechanical pulp, tensile strength

1975-218

特別講演、
これからのウッドケミカルスおよび無公害パルプ化に関する最近の海外の研究の動向

中野準三
東京大学農学部

Invited lecture:
Recent research trends in wood chemicals and pollution-free pulping in foreign countries

Junzo Nakano
Faculty of Agriculture, the University of Tokyo

第21回（1976.10.18-19）東京大学農学部

1976-101
成育時の光質とリグニン
田中治郎
林業試験場
Relation between light quality and lignin structure during growth
Jiro Tanaka
Government Forest Products Research Institute
Keywords: *Platanus occidentalis*, environmental factor, S/V ratio, wave length,

1976-102
木材腐朽菌によるリグニンモデル化合物の代謝
西田篤実、福住俊郎
東京大学農学部
Metabolism of lignin model compounds by wood rotting fungi
Atsumi Nishida, Toshio Fukuzumi
Faculty of Agriculture, the University of Tokyo
Keywords: white-rot fungi, *Trametes* sp., ferulic acid, *p*-coumaric acid, UV spectrometry

1976-103
バクテリアによるリグニンモデル化合物の分解（III）
片山義博、福住俊郎
東京大学農学部
Degradation of lignin model compounds by bacteria (III)
Yoshihiro Katayama, Toshio Fukuzumi
Faculty of Agriculture, the University of Tokyo
Keywords: *Pseudomonas* sp., dehydrodiconiferyl alcohol. pinoresinol, guaiacylglycerol-β–coniferyl ether, ^{1}H-NMR, UV spectrometry

1976-104
Betulachrysoquinone hemiketal, A *p*-benzoquinone hemiketal type macrocyclic compound produced by *Phanerochaete chrysosporium*
C.-L. Chen[*1], H.-M. Chang[*1], T.K. Kirk[*2]
[*1]North Carolina State University, [*2]Forest Products Laboratory, USDA
Keywords: *Betula lutea*, fungal metabolite, ^{1}H-NMR, UV spectroscopy

1976-105
アミノベンゼンスルホン酸塩リグニンについて（V）
黒田健一[*1]、坂井克己[*2]、近藤民雄[*2]
[*1] 東京教育大学農学部、[*2] 九州大学農学部
On aminobenzenesulfonate lignin (V)
Ken-ichi Kuroda[*1], Kokki Sakai[*2], Tamio Kondo[*2]
[*1] Faculty of Agriculture, Tokyo University of Education, [*2]Faculty of Agriculture, Kyushu University
Keywords: vanillyl alcohol, sodium metanilate, ^{1}H-NMR, UV spectroscopy, IR spectroscopy

1976-106
クラフト蒸解時のイオウの挙動 第1報 蒸解条件とイオウの配分
近藤隆一郎、近藤民雄
九州大学農学部
Behavior of sulfur during kraft pulping (I), The distribution of sulfur into vapor-, liquid- and solid-phases during cooking
Ryuichiro Kondo, Tamio Kondo
Faculty of Agriculture, Kyushu University

Keywords: white bir*ch, Betula Tauschii*, sulfidity, gas chromatography, methyl mercapthane, dimethyl sulfide, dimethyl disulfide,

1976-107
ゲル浸透クロマトグラフィーによるカラマツアルカリリグニンの分子量分布測定（その 2）
香川詔士、小室益広
関東学院大学工学部
Determination of molecular weight distribution of larch alkali lignin by gel permeation chromatography (II)
Shoji Kagawa, Masuhiro Komuro
College of Engineering, Kanto Gakuin University
Keywords: larch, *Larix Kaempferi*, mass spectrometry,

1976-108
竹リグニンのエステル構造 -Coniferyl *p*−Coumarate の脱水素重合-
中村吉紀[*1]、樋口隆昌[*2]
[*1] 山陽国策パルプ株式会社、[*2] 京都大学木材研究所
Ester structure in bamboo lignin, −Dehydrogenative polymerization of coniferyl *p*-coumarate−
Yoshiki Nakamura[*1], Takayoshi Higuchi[*2]
[*1]Sanyo-Kokusaku Pulp Co. Ltd., [*2]Wood Research Institute, Kyoto University
Keywords: UV spectrometry, IR spectrometry, Zutropfverfahren, Zulaufverfahren

1976-109
ネズコ材のリグニンおよびリグナン
久津木英俊、塩 徹、樋口隆昌
京都大学木材研究所
Lignin and lignan in *Thuja Standishii*
Hidetoshi Kutsuki, Toru Shio, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: *Thuja plicata*, *O*-methyl transferase, dihydroxythujaplicatin, dihydroxythujaplicatin methyl ether, *S*-adenosylmethionine-$^{14}CH_3$,

1976-110
ユリノキ中のレジノール型リグナン類
藤本英人、樋口隆昌
京都大学木材研究所
Resinol type lignans in *Liriodendron tulipifera*
Hideto Fujimoto, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: pinoresinol, medioresinol, syringaresinol, lriodendrin, TLC, ^{1}H-NMR,

1976-111
ジオキサン・水によるリグニンの加水分解 −アルデヒド型フェニルクマラン2量体の単離
青山政和、榊原 彰
北海道大学農学部
Hydrolysis of lignin in dioxane-water, −Isolation of aldehyde type phenylcoumaran dimer
Masakazu Aoyama, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: Japanese oak, *Quercus crispula*, TLC, UV spectroscopy, IR spectroscopy, ^{1}H-NMR,

1976-112
圧縮あて材プロトリグニンの水素化分解 — 縮合型二量体の単離
安田征市、榊原 彰

北海道大学農学部
Hydrogenolysis of protolignin in compression wood, −Isolation of condensed type dimers
Seiichi Yasuda, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: larch, *Larix leptolepis,* mass spectrometry, IR spectroscopy, ^{1}H-NMR,

1976-113
リグニン水素化分解物の ^{13}C−NMR による検討
武山浩武、佐藤哲夫、榊原　彰
北海道大学農学部
Examination of lignin hydrogenolysis products by ^{13}C−NMR
Hirotake Takeyama, Tetsuo Sato, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: Yezo spruce, *Picea jezoensis*,

1976-114
Arundo donax, *Welwitschia bainessi* 及び関連物質の酸化分解
安田征市[*1]、G. E. Miksche[*2]
[*1] 北海道大学農学部、[*2]Lund Institute of Technology, Sweden
Oxidative degradation of *Arundo donax*, *Welwitschia bainessi* and related materials
Seiichi Yasuda[*1], G. E. Miksche[*2]
[*1]Faculty of Agriculture, Hokkaido University, [*2]Lund Institute of Technology, Sweden
Keywords: leaf lamina, petiole, permanganate oxidation, gas chromatography,

1976-115
シリンギル核リッチリグニンの単離
山崎　徹[*1]、幡　克美[*1]、樋口隆昌[*2]
[*1] 香川大学農学部、[*2] 京都大学木材研究所
Isolation of syringyl nucleus-rich lignin
Toru Yamasaki[*1], Katsumi Hata[*1], Takayoshi Higuchi[*2]
[*1]Faculty of Agriculture, Kagawa University, [*2]Wood Research Institute, Kyoto University
Keywords: mercury acetate, mercuration, MWL, nitrobenzene oxidation,

11976-116
総合討論：リグニン化学構造
座長: 寺島典二 (名古屋大学農学部)
General discussion: Structure of lignin
Moderator: Noritsugu Terashima (Faculty of Agriculture, Nagoya University)
Keywords:

1976-201
パルプの酸素酸化反応機構　反応速度論的研究
山田紹良、戸坂园夫、林　治助
北海道大学工学部
Reaction mechanism of oxygen oxidation of pulp, –Kinetic study
Akira Yamada, Kunio Tosaka, Jisuke Hayashi
Faculty of Engineering, Hokkaido University
Keywords: cellulose protectant, glucose, triethanolamine, magnesium sulfate, Mg-EDTA

1976-202
放射性同位元素標識リグニンの反応　−リグニンを構成する各炭素の酸素・アルカリ蒸解中の挙動（2）
荒木　広、寺島典二
名古屋大学農学部

Radiotracer experiments on lignin reactions, —The behavior of lignin carbons in oxygen-alkali pulping process (II)
Hiroshi Araki, Noritsugu Terashima
Faculty of Agriculture, Nagoya University
Keywords: oxygen-alkali pulping, radiotracer, radioisotope, carbon 14, pine, lignin, gel filtration,

1976-203
Dihydrodehydrodiisoeugenol の酸素・アルカリ酸化
沖 妙、大久保克美、石川久雄
愛媛大学農学部
Oxygen alkali oxidation of dihydrodehydrodiisoeugenol
Tae Oki, Katsumi Okubo, Hisao Ishikawa
Faculty of Agriculture, Ehime University
Keywords: UV spectrometry, difference spectrum, *o*-quinone

1976-204
非木材植物の酸化的脱リグニンについて
Tran van Ai、坂井克己、近藤民雄
九州大学農学部
On the oxidative delignification of certain non−woody plants
Tran van Ai, Kokki Sakai, Tamio Kondo
Faculty of Agriculture, Kyushu University
Keywords: *Oryza sativa, Hordeum vulgare*, *Phyllostachys pubescens*, *Saccharum officinarum*, sodium chlorite, Wise method

1976-205
クラフトパルプの酸素−オゾン漂白について
藤井利郎、上嶋 洋、赤松 勲
四国工業技術試験所
Oxygen-ozone bleaching of kraft pulp
Tosiro Fujii, Hiroshi Kamishima, Isao Akamatsu
National Industrial Research Institute of Shikoku
Keywords: Douglas fir, *Pseudotsuga taxifolia*, brightness, pH

1976-206
クラフトパルプのメタノール添加オゾン漂白
上嶋 洋、藤井利郎、赤松 勲
四国工業試験所
Bleaching of kraft pulp by ozone with addition of methanol
Hiroshi Kamishima, Tosiro Fujii, Isao Akamatsu
Government Industrial Research Institute, Shikoku
Keywords: cellulose protectant, brightness, breaking length, tear factor

1976-207
総合討論：酸化的脱リグニン
座長 近藤民堆 (九州大学農学部)
General discussion: Oxidative delignification
Moderator: Tamio Kondo (Faculty of Agriculture, Kyushu University)

1976-208
サルファイト系高歩留パルプの製造に関する研究 第 5 報 ディスクリファイニングによって露出する繊維表面
岩見田 糺[*1], 角 祐一郎[*1], 中野準三[*2]
[*1] 山陽国策パルプ株式会社, [*2] 東京大学農学部

Studies on production of sulfite chemimechanical pulps (V), Fiber surface exposed by disk-refining
Tadashi Iwamida[*1], Yuichiro Sumi[*1], Junzo Nakano[*2]
[1]Sanyo Kokusaku Pulp Co., Ltd., [*2] Faculty of Agriculture, the University of Tokyo,
Keywords: sulfite chemimechanical pulp, disk-refining, fiber surface, compound middle lamella, secondary wall, *Abies Mayriana*, *Betula Tauschii*, scanning electron microscopy,

1976-209
リグニンの塩素化アルカリ抽出（IX） 塩素化ジオキサンリグニン（CL）の 2，3 の物理化学的性質
河内進策
宮崎大学農学部
Chlorination of lignin followed by alkali extraction (IX), Physicochemical properties of chlorinated dioxane lignin
Sinsaku Kawachi
Faculty of Agriculture, Miyazaki University
Keywords: Japanese red pine, *Pinus densiflora*, dioxane lignin, viscosity, heat of wetting

1976-210
アカマツ材クラフト漂白廃液中の有機成分
島田謹爾
林業試験場
Organic components in bleaching effluent of red pine kraft pulp
Kinji Shimada
Government Forest Experiment Station
Keywords: *Pinus densiflora*, gas chromatography, mass spectrometry, alkali-copper dioxide oxidation,

1976-211
パルプ廃液の浄化に関する研究 —活性汚泥法による処理—
八重樫稔、三浦 清
北海道大学農学部
Studies on the purification of pulp mill effluent, —Treatment with activated sludge—
Minoru Yaegashi, Kiyoshi Miura
Faculty of Agriculture, Hokkaido University
Keywords: *Betula Tauschii*, Glehn’s spruce, *Picea Glehnii*. chromaticity, COD, BOD, TOC

1976-212
パルプスラッジから粒状活性炭の製造
品部義秋，国正秀昭
東洋パルプ株式会社
Manufacturing of granular activated carbon from pulp and paper sludge
Yoshiaki Shinabe, Hideaki Kunimasa
Toyo Pulp Co., Ltd.
Keywords: pulp and paper mills, organic sludges, granular activated carbon, adsorption, dry distillation

1976-213
紙パルプ排水水質モニタリングについての一方法
中村孝一，佐藤坦，福島正輝，秦邦男
十條製紙
A monitoring method of pulp and paper effluents
Koichi Nakamura, Taira Sato, Masateru Fukushima, Kunio Hata
Jujo Paper Co., Ltd.
Keywords: pulp and paper effluents, COD, BOD, continuous monitoring system, ultraviolet absorption method

1976-214
特別講演、紙・パルプ産業の現状と問題点

松井康博
十條製紙株式会社

Invited lecture:

Present state and future problems in pulp and paper industry

Yasuhiro Matsui
Jujo Paper Co. Ltd.

第22回（1977.10.8-9）北海道大学農学部

1977-101
DHP 合成に対する新しい試み
棚橋光彦、樋口隆昌
京都大学木材研究所
A new trial of synthesis of DHP
Mitsuhiko Tanahashi, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: dialysis membrane, cellulose tube, coniferyl alcohol, sinapyl alcohol, Zulaufverfahren, Zutropfverfahren

1977-102
グワヤシルグリセロール-β-グワヤシルエーテルと糖類の反応（第 2 報）
田中憲次、中坪文明、樋口隆昌
京都大学木材研究所
Reaction of guaiacylglycerol-β–guaiacyl ether and sugar (II)
Kenji Tanaka, Fumiaki Nakatsubo, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: LCC, lignin carbohydrate complex, quinone methide, gel filtration, ^{1}H-NMR

1977-103
コニフェリルアルコールと *d*-カテキンの脱水素共重合
小寺　学、棚橋光彦、樋口隆昌
京都大学木材研究所
Dehydrogenative copoymerization of coniferyl alcohol and *d*-catechin
Manabu Kodera, Mitsuhiko Tanahashi, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: molecular weight, UV spectroscopy, permanganate oxidation,

1977-104
リグニン生合成と側鎖飽和型フェノール成分
寺沢　実、三宅基夫
帯広畜産大学
Biosynthesis of lignin and phenolic components with saturated side chain
Minoru Terasawa, Motoo Miyake
Obihiro University of Agriculture and Veterinary Medicine
Keywords: *Betula platyphylla*, beturoside-^{14}C(U), platypylloside-^{14}C(U), phenylalanine-^{14}C(U), radio-tracer

1977-105
アメリカデイコリグニン生合成の特異性
久津木英俊、樋口隆昌
京都大学木材研究所
Specificity in lignin biosynthesis in *Erythrina crista-galli*
Hidetoshi Kutsuki, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: radio-tracer, ferulic acid-2-^{14}C, sinapic acid-2-^{14}C, acidolysis, TLC, poplar, *Pinus Thunbergii*

1977-106
デヒドロジコニフェリルアルコールの微生物分解
大田雅彦[*1]、樋口隆昌[*1]、岩原章二郎[*2]
[*1] 京都大学木材研究所、[*2]香川大学農学部
Degradation of dehydrodiconiferyl alcohol by microorganisms
Masahiko Ohta[*1], Takayoshi Higuchi[*1], Shojiro Iwahara[*2]

[*1]Wood Research Institute, Kyoto University, [*2] Faculty of Agriculture, Kagawa University

Keywords: biodegradation, *Fusarium* sp., phenylcoumaran substructures, ^{1}H-NMR,

1977-107

微生物によるコニフェリルアルコール脱水素重合物（DHP）の分解について

岩原章二郎[*1]、桑原正章[*1]、樋口　隆昌[*2]

[*1] 香川大学農学部、[*2]京都大学木材研究所

Degradation of dehydrogenative polymer of coniferyl alcohol (DHP) by microorganisms

Shojiro Iwahara[*1], Masaaki Kuwahara[*1], Takayoshi Higuchi[*2]

[*1]Faculty of Agriculture, Kagawa University, [*2]Wood Research Institute, Kyoto University

Keywords: biodegradation, *Fusarium* sp., gel filtration, pinoresinol, dehydrodiconiferyl alcohol

1977-108

微生物によるリグニン関連芳香族化合物の代謝

桑原正章、岩原章二郎

香川大学農学部

Metabolism of lignin related aromatic compounds by microorganisms

Masaaki Kuwahara, Shojiro Iwahara

Faculty of Agriculture, Kagawa University

Keywords: biodegradation, *Pseudomonas* sp., *Rhodotorula* sp., *Corynebacterium glutamicum*, demethoxylation

1977-109

木材腐朽菌の Benzoic acids，Cinnamic acids の還元酵素、及び Ferulic acid から Vanillic acid の生成酵素系について

西田篤実、福住俊郎

東京大学農学部

Reducing enzymes of benzoic acids and cinnamic acids in wood rotting fungi, and enzyme system converting ferulic acid to vanillic acid

Atsumi Nishida, Toshio Fukuzumi

Faculty of Agriculture, the University of Tokyo

Keywords: *Trametes* sp., 3,4,5-trimethoxybenzoic acid, gas chromatography

1977-110

アテ材化学成分の研究　—主として圧縮アテ材のリグニンについて—

榊原　彰[*1]、諸星紀幸[*2]、安田征市[*3]

[*1] 北海道大学農学部, [*2] 東京農工大学農学部, [*3] 名古屋大学農学部

Studies on the chemical components of reaction wood. –Lignin in compression wood

Akira Sakakibara[*1], Noriyuki Morohoshi[*2], Seiichi Yasuda[*3]

[*1]Faculty of Agriculture, Hokkaido University, [*2]Faculty of Agriculture, Tokyo University of Agriculture and Technology, [*3]Faculty of Agriculture, Nagoya University

Keywords: *Abies sachalinensis, Larix leptolepis, Fraxinus mandshurica*, lariciresinol *p*-coumarate, *p*-hydroxyphenyl unit

1977-111

Mäule 反応の呈色機構（第 8 報）

飯塚堯介、中野準三

東京大学農学部

Mechanism of Mäule color reaction (VIII)

Gyosuke Meshitsuka, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords: lignin model compound, ESR spectroscopy, visible light absorption spectroscopy chlorinated *o*-quinone,

1977-112

トレーサー法によるリグニンの諸反応の解析 —パルプ化過程におけるフェニルプロパン側鎖末端基の挙動—

荒木 広、富村洋一、寺島典二

名古屋大学農学部

Radiotracer experiments on lignin reactions, -The behaviour of phenylpropane side-chain carbons during pulping process—

Hiroshi Araki, Yoichi Tomimura, Noritsugu Terashima

Faculty of Agriculture, Nagoya University

Keywords; radiotracer, radioisotope, carbon 14, pine, lignin, kraft pulping, soda pulping, oxygen-alkali pulping, gel filtration,

1977-113

三弗化硼素、フェノール系におけるリグニン及びリグニンモデル化合物の反応

船岡正光、阿部 勲

三重大学農学部

Reaction of lignin and lignin model compounds in boron trifluoride and phenol system

Masamitsu Funaoka, Isao Abe

Faculty of Agriculture, Mie University

Keywords; diphenylmethane, catechol, nucleus exchange reaction

1977-114

中性での H_2O_2 酸化によるリグニンの淡色化について

石川久雄、沖 妙、大久保克美

愛媛大学農学部

Lignin color reduction by H_2O_2 oxidation in neutral condition

Hisao Ishikawa, Tae Oki, Katsumi Okubo

Faculty of Agriculture, Ehime University

Keywords; lignosulfonic acid, thiolignin, dioxane lignin, MWL, reductive bleaching, zinc dithionite, *o*-quinone, *p*-quinone

1977-115

過酸化物および酸素・アルカリによるリグニン酸化分解の特徴

沖 妙、大久保克美、石川久雄

愛媛大学農学部

Specificity in oxidative degradation of lignin by peroxide and oxygen alkali

Tae Oki, Katsumi Okubo, Hisao Ishikawa

Faculty of Agriculture, Ehime University

Keywords; lignin model compounds, dioxane lignin, peracetic acid, hydrogen peroxide

1977-116

総合討論:

座長: 樋口隆昌（京都大学木材研究所）

General discussion:

Moderator: Takayoshi Higuchi (Wood Research Institute, Kyoto University)

1977-201

リグニン及びリグニンモデル化合物のオゾン分解

金子英信、細谷修二、中野準三

東京大学農学部

Degradation of lignin and lignin model compounds by ozone

Hidenobu Kaneko, Shuji Hosoya, Junzo Nakano

Faculty of Agriculture, the University of Tokyo

Keywords; guaiacylglycerol-β-guaiacyl ether, TLC, HPLC, ^{1}H-NMR, ^{13}C-NMR

1977-202
針葉樹リグニンモデル化合物のオゾン分解
小島康夫、三浦　清、香山　彊
北海道大学農学部
Degradation of softwood lignin model compounds by ozone
Yasuo Kojima, Kiyoshi Miura, Tsutomu Kayama
Faculty of Agriculture, Hokkaido University
Keywords; UV spectrometry, IR spectrometry, TLC, ^{1}H-NMR, ^{13}C-NMR

1977-203
液相法によるパルプのオゾン漂白
藤井利郎、上嶋　洋、赤松　勲
四国工業技術試験所
Ozone bleaching of pulp in liquid phase
Toshiro Fujii, Hiroshi Kamishima, Isao Akamatsu
Government Industrial Research Institute, Shikoku
Keywords; Douglas fir, *Pseudotsuga taxifolia*, cellulose protectant, gas phase bleaching

1977-204
クラフトパルプのオゾン漂白におけるメタノールのセルロース保護機構に関する研究
上嶋　洋、藤井利郎、赤松　勲
四国工業技術試験所
Mechanism of protection of cellulose by methanol during ozone bleaching of kraft pulp
Hiroshi Kamishima, Toshiro Fujii, Isao Akamatsu
Government Industrial Research Institute, Shikoku
Keywords; Douglas fir, *Pseudotsuga taxifolia*, *n*-hexane, ethyl acetate, acetone methyl oxalate, pyridine, methyl cellosolve

1977-205
RGP のオゾン及びアルカリによる後処理
小林　武、細川　純、久保隆昌、木村　裕
四国工業技術試験所
Posttreatment of RGP with ozone and alkali
Takeshi Kobayashi, Jun Hosokawa, Takamasa Kubo, Yutaka Kimura
Government Industrial Research Institute, Shikoku
Keywords;

1977-206
酸素・アルカリ蒸解におけるリグニンの挙動について
青柳哲夫、細谷修二、中野準三
東京大学農学部
Behavior of lignin during oxygen alkali pulping
Tetsuo Aoyagi, Shuji Hosoya, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords; lignin model compounds, TLC, mass spectrometry, ^{1}H-NMR, ^{13}C-NMR

1977-207
亜硫酸ソーダ—酸素・アルカリ蒸解について
幡　克美、林　忠和、十河村男、山崎　徹
香川大学農学部
On the sodium sulfite-oxygen/alkali pulping
Katsumi Hata, JongHer Lin, Murao Sogo, Toru Yamasaki
Faculty of Agriculture, Kagawa University
Keywords; beech, *Fagus crenata*, *Eucalyptus* sp. physical properties of NS-OA pulp

1977-208
クラフト蒸解におけるリグニン中へのイオウの取り込み
石野良明、近藤隆一郎、近藤民雄
九州大学農学部
Introduction of sulfur into lignin during kraft pulping
Yoshiaki Ishino, Ryuichiro Kondo, Tamio Kondo
Faculty of Agriculture, Kyushu University
Keywords; Japanese red pine, *Pinus densiflora*, hydrogen sulfide, sulfidation of wood, wood sulfide

1977-209
クラフト蒸解時のイオウの挙動（III）—揮発性有機イオウ化合物の生成について—
近藤隆一郎、近藤民雄
九州大学農学部
Behavior of sulfur during kraft pulping (III), On the formation of volatile organic sulfur compounds
Ryuichiro Kondo, Tamio Kondo
Faculty of Agriculture, Kyushu University
Keywords; *Betula Tauschii, Pinus densiflora*, dioxane lignin, lignin model compound, methyl mercaptane, dimethyl sulfide, dimethyl disulfide, demethylation reaction

1977-210
SOX 法によるバガスのパルプ化
御田昭雄[*1]、佐伯　剛[*2]
[*1] 東京工業試験所、[*2] 工学院大学
Pulping of bagasse by SOX process
Akio Mita[*1], Tsuyoshi Saiki[*2]
[*1]Government Chemical Industrial Research Institute, Tokyo, [*2]Kogakuin University
Keywords; cooking with ($Na_2SO_4 + SO_2$), soda pulping, electron microscopy

1977-211
SO_2＋$MgSO_4$ 2 成分蒸解法に関する研究 「広葉樹の木材細胞壁の porous 構造と溶出リグニンの分子量特性」
鈴木　勉、戸坂園夫、林　治助
北海道大学工学部
Studies on two component pulping with SO_2＋ $MgSO_4$. “Relation between porous structure of hardwood cell wall and molecular weight characteristics of dissolved lignin”
Tsutomu Suzuki, Kunio Tosaka, Jisuke Hayashi
Faculty of Engineering, Hokkaido University
Keywords; *Betula Ermanii*, pore volume, gel filtration, cell wall morphology

1977-212
マグネシャ系吸着剤を中心にした NSCP 廃水の処理
猪狩淑将[*1]、横山正一郎[*1]、板矢柳太郎[*2], 池田恵一[*2]、大熊恒雄[*2]、
加藤啓介[*3]、深川和幸[*3]
[*1] 東京工業試験所、[*2]北曹、[*3]住重エンバイロ
Processing of NSCP effluent with magnesia adsorbent
Yoshimasa Ikari[*1],Shoichiro Yokoyama[*1],Ryutaro Itaya[*2], Kei-ichi Ikeda[*2], Tsuneo Okuma[*2], Keisuke Kato[*3], Kazuyuki Fukagawa[*3]
[*1]Government Chemical Industrial Research Institute, Tokyo, [*2]Hokuso Co. Ltd., [*3]Sumijyu Environmental Engineering Co. Ltd.
Keywords; COD, chromaticity, TOC, activated sludge

1977-213

クラフトパルプ廃水、アルカリチオリグニン、リグニンモデル物質の石灰による凝集処理
赤松　勲、上嶋　洋、藤井利郎、細川　純
四国工業技術試験所
Coagulation treatments with lime of effluent from kraft pulp mill, alkali thiolignin, and lignin model compounds
Isao Akamatsu, Hiroshi Kamishima, Toshiro Fujii, Jun Hosokawa
Government Industrial Research Institute, Shikoku
Keywords;　curcumin, tin, zinc, dehydrodiisoeugenol

1977-214
総合討論:
座長: 中野準三
東京大学農学部
General discussion:
Moderator: Junzo Nakano
Faculty of Agriculture, the University of Tokyo

1977-215
特別講演:
フアインケミカルスを中心としたリグニン利用の将来
岡部次郎
山陽国策パルプ株式会社
Invited lecture:
Future aspects of utilization of lignin as fine chemicals
Jiro Okabe
Sanyo-Kokusaku Pulp Co. Ltd.
Keywords:　water-reducing admixtures, granulation agent for ore powder, cement detergent,

第23回（1978.11.1-2）愛媛大学農学部

1978-101
シナップ酸形成能の高いコノテガシワ *O*−メチル基転位酵素について
久津木英俊、島田幹夫、樋口隆昌
京都大学木材研究所
O-Methyl transferase in*Thuja orientalis* having high sinapic acid forming ability
Hidetoshi Kutsuki, Mikio Shimada, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: substrate specificity, metal ion demand, optimum pH, Michaelis constant

1978-102
透析膜法による DHP の合成
棚橋光彦、樋口隆昌
京都大学木材研究所
Synthesis of DHP by the dialysis membrane method
Mitsuhiko Tanahashi, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: Zulaufverfahren, Zutropfverfahren, coniferyl alcohol, sinapyl alcohol, LCC, cell wall model

1978-103
木材腐朽菌による針葉樹、広葉樹型リグニンの分解に見られるシリンギル核劣化の優先性
野口明雄^{*1}、島田幹夫^{*1}、樋口隆昌^{*1}、青島清雄^{*2}
^{*1}京都大学木材研究所、^{*2}林業試験場
Preferential degradation of syringyl nucleus in decay of softwood and hardwood lignin by wood- rotting fungi
Akio Noguchi^{*1}, Mikio Shimada^{*1}, Takayoshi Higuchi^{*1}, Kiyoo Aoshima^{*2}
^{*1}Wood Research Institute, Kyoto University,^{*2}Forestry and Forest Products Research Institute
Keywords: *Coriolus versicolor, Poria subacida, Tyromyces palustris*, host specificity, radio-labeled lignin model compounds,

1978-104
リグニン生分解への立体生化学的アプローチ：ラッカーゼのリグニン側鎖不斉構造に及ぼす非立体特異的酸化反応の意義
島田幹夫、野口明雄、樋口隆昌
京都大学木材研究所
Biostereochemical approaches to lignin biodegradation: Meaning of non-stereo specific oxidation reaction on asymmetric side chain structure of lignin by laccase
Mikio Shimada, Akio Noguchi, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: *Coriolus versicolor*, ^{3}H-coniferyl alcohol, ^{3}H/^{14}C-coniferyl alcohol, ^{3}H/^{14}C-DHP,

1978-105
グアヤシルグリセロール-β-コニフェリルエーテルの微生物分解（第2報）
片山健至、中坪文明、樋口隆昌
京都大学木材研究所
Microbial degradation of guaiacylglycerol-β–coniferyl ether (II)
Takeshi Katayama, Fumiaki Nakatsubo, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: *Fusrium solani*, TLC, ^{1}H-NMR, UV spectrometry

1978-106
デヒドロジコニフェリールアルコールの酵素的酸化について
岩原章二郎^{*1}、西平 強^{*1}、城森孝仁^{*1}、桑原正章^{*1}、樋口隆昌^{*2}
^{*1}香川大学農学部, ^{*2}京都大学木材研究所

Enzymatic oxidation of dehydrodiconiferyl alcohol
Shojiro Iwahara[*1], Tsuyoshi Nishihira[*1], Takahito Jomori[*1], Masaaki Kuwahara[*1], Takayoshi Higuchi[*2]
[*1]Faculty of Agriculture, Kagawa University, [*2]Wood Research Institute, Kyoto University
Keywords: *Fusarium* spp. gel filtration, TLC,

1978-107
糸状菌および細菌によるリグニン関連芳香族化合物の代謝
桑原　正章、登林浩司、佐藤哲雄、岩原章二郎
香川大学農学部
Metabolism of lignin related aromatic compounds by fungi and bacteria
Masaaki Kuwahara, Koji Noboribayashi, Tetsuo Sato, Shojiro Iwahara
Faculty of Agriculture, Kagawa University
Keywords: *Pseudomonas sp., Fusarium solani, Fusarium oxysporum, Phanerochaete chrysosporium,* differential respirometer,

1978-108
カラマツの phenylpropane 誘導体および関連物質
三木啓司、笹谷宜志、榊原　彰
北海道大学農学部
Phenylpropane derivatives and related compounds from *Larix Kaempferi*
Keiji Miki, Takashi Sasaya, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: larch, *Larix Kaempferi*, inner bark, UV spectroscopy, ^{1}H-NMR,

1978-109
ジオキサン・水によるリグニンの加水分解　—ラクトン環を有する化合物の単離—
青山政和、榊原　彰
北海道大学農学部
Hydrolysis of lignin by dioxane-water, –Isolation of compounds having lactone ring—
Masakazu Aoyama, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: Japanese oak, *Quercus crispula*, IR spectroscopy, mass spectrometry, ^{1}H-NMR,
1978-110
プロトリグニンの水素化分解に関する研究　—新 3 量体の単離—
保田智之、榊原　彰
北海道大学農学部
Studies on the hydrogenolysis of protolignin, -Isolation of a new trimer—
Yasuda Tomoyuki, Ajira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: larch, *Larix Kaempferi*, compression wood, matairesinol, IR spectroscopy, mass spectrometry, ^{1}H-NMR,

1978-111
リグニンの化学構造の不均質性に関する研究
富村洋一、横井達明、寺島典二
名古屋大学農学部
Studies on the heterogeneity of lignin structure
Yooichi Tomimura, Tatsuaki Yokoi, Noritsugu Terashima
Faculty of Agriculture, Nagoya University
Keywords: *Pinus Thunbergii*, Kamabuchi poplar (Populus nigra X Populus Maximowiczii), radiotracer, ^{3}H,^{14}C, double labeling

1978-112
MWL より分離した LCC 中のリグニンと糖の結合様式について

榎　章郎、有国　尚、越島哲夫
京都大学木材研究所
Linkages between lignin and carbohydrates in LCC isolated from MWL
Akio Enoki, Hisashi Arikuni, Tetsuo Koshijima
Wood Research Institute, Kyoto University
Keywords: *Pinus densiflora*, enzymatic degradation, Seruroshin, boron tribromide,

1978-113
β-アルコキシ脱離反応を用いたアリールグリセロール-β-アリールエーテル結合の選択的開裂
松本雄二、石津　敦、中野準三
東京大学農学部
Selective cleavage of arylglycerol-β-aryl ether bond by β-alkoxy elimination reaction
Yuji Matsumoto, Atsushi Ishizu, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: *erythro* and *threo* isomers, ^{13}C-NMR, mass spectrometry, TLC

1978-114
三弗化硼素・フエノール系におけるリグニンの反応　—ジフェニルメタン構造の形成について
船岡正光、阿部　勲
三重大学農学部
Reaction of lignin in borontrifluoride-phenol system. –Formation of diphenylmethane structure
Masamitsu Funaoka, Isao Abe
Faculty of Agriculture, Mie University
Keywords: Yezo spruce, *Picea jezoensis*, TLC, quinone methide, quinhydron, visible light absorption spectrometry

1978-115
過マンガン酸カリ酸化分解によるリグニン化学構造の分析
諸星紀幸[*1]、W. G. Glasser[*2]
東京農工大学農学部
Analysis of lignin structure by oxidative degradation with potassium permanganate
Noriyuki Morohoshi[*1], W.G. Glasser[*2]
[*1]Faculty of Agriculture, Tokyo University of Agriculture and Technology, [*2]Virginia Polytechnic Institute and State University
Keywords: Loblolly pine, *Pinus taeda*, red alder, *Alnus rubra*, gel filtration, gas chromatography

1978-116
アルカリリグニンの着色構造　—バニリルアルコール縮合物の着色構造について—
安田征市、藤井和美、尹　炳虎、寺島典二
名古屋大学農学部
Chromophoric structures of alkali lignin. Chromophoric structures of condensation products from vanillyl alcohol
Seiichi Yasuda, Kazumi Fujii, Byung-Ho Yoon, Noritsugu Terashima.
Faculty of Agriculture, Nagoya University
Keywords: ^{13}C-enrichment, ^{13}C-NMR, diguaiacyl methane, quinone methide,

1978-117
核共役二重結合を有する化合物の過酸化水素に対する挙動
小島康夫、香山　彊
北海道大学農学部
Behavior of aromatic compounds carrying conjugated double bonds in the reaction with hydrogen peroxide
Yasuo Kojima, Tsutomu Kayama
Faculty of Agriculture, Hokkaido University
Keywords: isoeugenol, dehydrodiisoeugenol, vanillin, *o*-methoxy-*p*-hydroquinone, mass spectrometry,

^{1}H-NMR,

1978-201
高濃度オゾン水によるクラフトパルプの漂白
藤井利郎[*1]、上嶋 洋[*1]、赤松 勲[*1]、中山繁樹[*2]、難波敬典[*2]
[*1] 四国工業技術試験所、[*2] 三菱電機株式会社
Bleaching of kraft pulp with water containing high concentration of ozone
Toshiro Fujii[*1], Hiroshi Kamishima[*1], Isao Akamatsu[*1], Shigeki Nakayama[*2], Takanori Nanba[*2]
[*1]Government Industrial Research Institute, Shikoku, [*2]Mitsubishi Electric Corporation
Keywords: Douglas fir, *Pseudotsuga taxifolia*, brightness, viscosity, pH

1978-202
高収率パルプの製造に関する研究（第 3 報）TMP のオゾン処理に及ぼすリファイニング温度の影響
久保隆昌、細川 純、小林 武、赤松 勲、木村 裕
四国工業技術試験所
Studies on the high yield pulp production (III), Effect of refining temperature on ozone treatment of TMP
Takamasa Kubo, Jun Hosokawa, Takeshi Kobayashi, Isao Akamatsu, Yutaka Kimura
Government Industrial Research Institute, Shikoku
Keywords: Japanese red pine, *Pinus densiflora*, freeness, fiber length distribution, breaking length

1978-203
酸素酸化精製パルプのオゾン漂白について（第 2 報）
萱場 基、戸坂圀夫、林 治助
北海道大学工学部
Ozone bleaching of oxygen treated pulp (II)
Motoi Kayaba, Kunio Tosaka, Jisuke Hayashi
Faculty of Engineering, Hokkaido University
Keywords: *Betula Tauschii*, brightness,

1978-204
チオリグニンのオゾン分解について
金子英信、細谷修二、中野準三
東京大学農学部
Degradation of thiolignin by ozone
Hidenobu Kaneko, Shuji Hosoya, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: ESR spectroscopy, double bond content, GPC, IR spectroscopy, ^{1}H-NMR,

1978-205
クラフト蒸解時のイオウの挙動（IV） 揮発性有機イオウ化合物の生成について
近藤隆一郎、近藤民雄
九州大学農学部
Behavior of sulfur during kraft pulping (IV), On the formation of volatile organic sulfur compounds
Ryuichiro Kondo, Tamio Kondo
Faculty of Agriculture, Kyushu University
Keywords: *Betula Tauschii*, *Pinus densiflora,* labile methoxyl group, dioxane lignin

1978-206
放射線前照射チップのクラフト蒸解に関する研究
稲葉政満、飯塚堯介、中野準三
東京大学農学部
Studies on the kraft pulping of wood chips pretreated byγ-ray
Masamitsu Inaba, Gyosuke Mashitsuka, Junzo Nakano
Faculty of Agriculture, the University of Tokyo

Keywords: beech, *Fagus crenata*, α-hydroxylalkyl radical

1978-207
アルカリ蒸解助剤テトラヒドロアントラキノンの脱リグニン促進機構
矢口時也[*1]、佐藤惇夫[*1]、野村芳禾[*1]、中村正人[*1]、細谷修二[*2]、中野準三[*2]
[*1] 本州製紙株式会社、[*2] 東京大学農学部
Promotion mechanism of delignification by alkaline cooking aids, tetrahydroanthraquinone
Tokiya Yaguchi[*1], Atsuo Satoh[*1], Yoshika Nomura[*1], Masato Nakamura[*1], Shuji Hosoya[*2], Junzo Nakano[*2]
[*1]Honshu Paper Co. Ltd. [*2]Faculty of Agriculture, the University of Tokyo
Keywords: guaiacylglycerol-β–guaiacyl ether, oxygen-free cooking, carbohydrate

1978-208
ユーカリ材の抽出成分量とパルプ収率
亀井基和[*1]、大江礼三郎[*2]
[*1] 北越製紙株式会社、[*2] 東京農工大学農学部
Content of extractives and yield of pulp from eucalyptus wood
Motokazu Kamei[*1], Raysaburo Oye[*2]
[*1]Hokuetsu Paper Co. Ltd., [*2]Faculty of Agriculture, Tokyo University of Agriculture and Technology
Keywords: *Eucalyptus calophylla*, *Eucalyptus diversicolor,* Klason lignin

1978-209
酸素・アルカリ蒸解の蒸解要因(II)界面活性剤添加の効果
日黒貞利、近藤民雄
九州大学農学部
Cooking factor in oxygen alkali pulping (II), Effect of addition of surface active agents
Sadatoshi Meguro, Tamio Kondo
Faculty of Agriculture, Kyushu University
Keywords: *Betula Tauschii*, Asplund pulp, sodium laurylbenzene sulfonate, Tween 20

1978-210
マグネファイト—酸素・Mg(OH)2 蒸解について
十河村男、幡 克美、山崎 徹
香川大学農学部
On the magnefite-O2+Mg(OH)2 pulping
Murao Sogo, Katsumi Hata, Toru Yamasaki
Faculty of Agriculture, Kagawa University
Keywords: *Betula Tauschii*, *Eucalyptus* sp., gel filtration, MWL

1978-211
非木材繊維の叩解について(第 2 報)
ラム・チ・パクチュエト[*1]、原 啓志[*2]、大江礼三郎[*1]
[*1] 東京農工大学農学部、[*2] 三島製紙株式会社
Beating of non-woody fiber (II)
Lam T. B. T[*1]., Keishi Hara[*2], Raysabro Oye[*1]
[*1]Faculty of Agriculture, Tokyo University of Agriculture and Technology, [*2]Mishima Paper Co., Ltd.
Keywords: *Linum usitatissimum, Hibiscus cannabinus*, mercury penetration, monosaccharide composition

1978-212
バガスから新聞紙パルプの調製について
御田昭雄[*1]、佐伯 剛[*2]
東京工業試験所、工学院大学
Production of newspaper pulp from bagasse
Akio Mita[*1], Tsuyoshi Saiki[*2]
[*1]Government Chemical Industrial Research Institute, Tokyo, [*2]Kogakuin University

Keywords: bleaching, brightness, breaking length, tear factor, percent Elmendorf tear factor, folding endurance

1978-213
TMP 法によるバガスのパルプ化
西山昌史[*1]、松尾隆吉[*1]、小林良生[*1]、佐藤隆士[*2]、Naiyana Niyomwan[*3]
[*1] 四国工業技術試験所、[*2] 日立造船株式会社、[*3]ASRCT
Pulping of bagasse by TMP process
Masashi Nishiyama[*1], Ryukichi Matsuo[*1], Yoshinari Kobayashi[*1], Takashi Sato[*2], Naiyana Niyomwan[*3]
[*1]Government Industrial Research Institute, Shikoku, [*2]Hitachi Zosen Corporation, [*3]ASRCT
Keywords: freeness, breaking length, tear factor,

1978-2014
KP 晒廃液中の毒性物質の分画とキャラクタリゼーション
鮫島一彦[*1]、B. Simson[*2], C. W. Dence[*2]
[*1] 高知大学農学部、[*2] ニューヨーク州立大学
Fractionation and characterization of toxic substances in effluent from KP bleaching process
Kazuhiko Sameshima[*1], B. Simon [*2], C.W. Dence [*2]
[*1]Faculty of Agriculture, Kochi University, [*2]State University of New York.
Keywords: southern pine, *Daphnia magna*, *Aspergillus fumigatus*, TOC, molecular weight, VPO

1978-215
KP 蒸解廃液の活性汚泥処理と限外ロ過特性について
三浦　清、平田裕浩
北海道大学農学部
Active sludge treatment of KP waste liquor and its ultrafiltration characteristics
Kiyoshi Miura, Yasuhiro Hirata
Faculty of Agriculture, Hokkaido University
Keywords: *Betula platyphylla, Picea Glehnii*, BOD, COD, UV and visible light absorption,

1978-216
Mg 系吸着剤のパルプ廃液成分吸着能
猪狩俶将、横山正一郎
東京工業試験所
Adsorption capacity of Mg containing adsorbents for components in pulp mill effluent
Yoshimasa Ikari, Shoichiro Yokoyama
Government Chemical Industrial Research Institute, Tokyo
Keywords: COD, adsorption isotherm,

1978-217
活性炭吸着機構に及ぼすパルプ製造排水成分の物理化学的性状の影響
飯山賢治、中野準三
東京大学農学部
Effect of physicochemical properties of pulp mill effluent on the mechanism of adsorption by activated carbon
Kenji Iiyama, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: softwood lignin sulfonic acid, molecular size, intrinsic viscosity, adsorption isotherm

1978-218
特別講演、高収率パルプの現状と問嘩点
角祐一郎
山陽国策パルプ株式会社
Invited lecture:

Present state and problems in high yield pulp production

Yuichiro Sumi
Sanyo-Kokusaku Pulp Co. Ltd.

Keywords: SCP, TMP, NSSC, brightness, Tampella process, SCA-Billerud process, Ebara process

第24回（1979.11.1-2）京都大学、生産開発科学研究所

1979-101
β-*O*-4 及びシリンガレジノール構造からなる三量体リグニンモデル化合物の合成
釜谷保志、中坪文明、樋口隆昌
京都大学木材研究所
Synthesis of a trimeric lignin model compound composed of β-O-4 and syringaresinol substructures
Yasushi Kamaya, Fumiaki Nakatsubo, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: stereochemistry, *erythro* and *threo* isomers, IR spectroscopy, ^{1}H-NMR

1979-102
β-*O*-4 及び β-1 構造からなる三量体リグニンモデル化合物の合成
難波宏彰、中坪文明、樋口隆昌
京都大学木材研究所
Synthesis of a trimeric lignin model compound composed of β-O-4 and β-1 substructures
Hiroaki Namba, Fumiaki Nakatsubo, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: IR spectroscopy, UV spectroscopy, ^{1}H-NMR,

1979-103
フェニルクマラン及び β-1 構造からなる三量体リグニンモデル化合物の合成並びにリグニンモデル化合物の合成に関するまとめ
中坪文明、樋口隆昌
京都大学木材研究所
Synthesis of trimeric lignin model compounds composed of phenylcoumaran and β-1 substructures, and summary of synthetic method for lignin model compounds
Fumiaki Nakatsubo, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: IR spectroscopy, ^{1}H-NMR, diastereomers,

1979-104
広葉樹プロトリグニンの水素化分解に関する研究　-新 2 量体（γ-*O*-4）の単離
黄　炳浩、榊原　彰
北海道大学農学部
Studies on the hydrogenolysis of hardwood protolignin. –Isolation of a new dimeric product with γ-*O*-4 linkage
Byung Ho Hwang, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: *Fraxinus excelsissima*, TLC, UV spectrum, IR spectrum, MS spectrum, ^{1}H-NMR,

1979-105
リグナン類の ^{13}C−NMR スペクトル
三木啓司、笹谷宣志、榊原　彰
北海道大学農学部
^{13}C−NMR spectroscopy of lignans
Keiji Miki, Takashi Sasaya, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: larch, *Larix Kaempferi*, diastereomer, *erythro* and *threo* isomers, chemical shift

1979-106
ユウガオ及びヒョータン硬化果皮のリグニンについて
川上日出国、福田忠徳
名古屋大学農学部
On the lignin in hardened rind of *Lagenaria siceraria Standley var. hispida Hara* and *Lagenaria siceraria*

Standley var. gourd Hara
Hidekuni Kawakami, Tadanori Fukuda
Faculty of Agriculture, Nagoya University
Keywords: phenylalanine ammonia-lyase, nitrobenzene oxidation, permanganate oxidation, ethanolysis, ^{13}C-NMR, lignin structure

1979-107
出土木材リグニンの化学構造
玉井　篤、井上嘉幸、南　享二
筑波大学農林工学系
Chemical structure of lignin in excavated wood
Atsushi Tamai, Yoshiyuki Inoue, Kyoji Minami
Institute of Agricultural and Forest Engineering, University of Tsukuba
Keywords: *Aesculus turbinate*, MWL, permanganate oxidation, ^{1}H-NMR, nitrobenzene oxidation

1979-108
透析膜法による LCC の合成と植物細胞壁のモデル化
棚橋光彦、樋口隆昌
京都大学木材研究所
Synthesis of LCC by dialysis membrane method and modeling of plant cell wall
Mitsuhiko Tanahashi, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: *Phyllostachys pubescens*, thermal softening property, hydrophobic chromatography,
1979-109
リグニン・糖結合体に関する研究（その 2）リグニン・糖結合体に及ぼす界面活性剤の効果
東　順一、高橋信義、越島哲夫
京都大学木材研究所
Studies on lignin-carbohydrate complex (II), Effect of surface active agents on lignin-carbohydrate complex
Junichi Azuma, Nobuyoshi Takahashi, Tetsuo Koshijima
Wood Research Institute, Kyoto University
Keywords: Japanese red pine, *Pinus densiflora*, gel filtration, non-ionic detergent, anionic detergent, cationic detergent

1979-110
二量体に相当するリグニンモデル化合物の酸化分解
沖　妙、大久保克美、石川久雄
愛媛大学農学部
Oxidative degradation of lignin model compounds corresponding to dimer
Tae Oki, Katsumi Okubo, Hisao Ishikawa
Faculty of Agriculture, Ehime University
Keywords: guaiacylglycerol-β-guaiacyl ether, dihydrodehydrodiisoeugenol, symprocosigenol, oxygen-alkali oxidation, alkaline H_2O_2 oxidation, peracetic acid oxidation

1979-111
リグニンの主分散及びローカルモード緩和
畠山兵衛[*1]、中村邦雄[*2]、畠山立子[*3]
[*1] 製品科学研究所、[*2] 神奈県工業試験所、[*3] 繊維高分子材料研究所
Main dispersion and local mode relaxation of lignin
Hyoe Hatakeyama[*1], Kunio Nakamura[*2], Tatsuko Hatakeyama[*3]
[*1]Industrial Products Research Institute, [*2]Industrial Research Institute of Kanagawa Prefecture, [*3]Research Institute for Polymers and Textiles.
Keywords: lignin related polystyrenes, MWL, GPC, broad-line NMR, DSC, glass transition temperature

1979-112
細胞間層リグニンの性状について

趙　南爽、飯塚堯介、中野準三
東京大学農学部
On the characteristics of compound middle lamella lignin
Nam Seok Cho, Gyosuke Meshitsuka, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: *Betula Ermanii*, MWL, nitrobenzene oxidation, S/V ratio,

1979-113
リグニンのオゾン分解
金子英信、細谷修二、中野準三
東京大学農学部
Degradation of lignin with ozone
Hidenobu Kaneko, Shuji Hosoya, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: dehydrodivanillyl alcohol, thiolignin, *Picea jezoensis*, soda lignin, TLC, ^{1}H-NMR, ^{13}C-NMR

1979-114
リグニンの親水性化に関する研究（2）
飯塚堯介、中野準三
東京大学農学部
Studies on introducing hydrophilicity to lignin (II)
Gyosuke Meshitsuka, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: softwood kraft lignin, sulfonation, surface tension, metal complex formation
1979-115
クラフトリグニンの調製について ― 失敗の記録から
中野準三、高塚千代子
東京大学農学部
Preparation of kraft lignin, –Problems in purification procedure
Junzo Nakano, Chiyoko Takatsuka
Faculty of Agriculture, the University of Tokyo
Keywords: methoxyl content, dioxane, freeze drying

1979-116
特別講演、
Invited lecture:
Speculative pathways for the fungal metabolism of lignin substructures
T. K. Kirk
Forest Products Laboratory, Madison, U.S.A
Keywords: white-rot fungi, *Phanerochaete chrysosporium*, *Fusarium* sp.,

1979-201
針葉樹リグニンと広葉樹リグニンの担子菌による分解
広居忠量
林業試験場
Degradation of softwood lignin and hardwood lignin by *Basidiomycetes*
Tadakazu Hiroi
Forestry and Forest Products Research Institute
Keywords: *Chamaecyparis obtuse, Betula Tauschii*, *Pinus densiflora, Fagus crenata,* MWL, *Phanerochaete chrysosporium*,

1979-202
カタウロコタケ粗酵素によるリグニンの分解
福田　滋、原口隆英、諸星紀幸

東京農工大学農学部
Degradation of lignin by crude enzyme of *Stereum flustulosum*
Shigeru Fukuda, Takafusa Haraguchi, Noriyuki Morohoshi
Faculty of Agriculture, Tokyo University of Agriculture and Technology
Keywords: *Picea jezoensis, Ulmus davidiana,* MWL, Bavendamm's reaction, vanillic acid, ferulic acid

1979-203
Fusarium spp. によるリグニン関連芳香族化合物の側鎖の分解について
岩原章二郎[*1]、城森孝仁[*1]、一色健二[*1]、樋口隆昌[*2]
香川大学農学部, 京都大学木材研究所
Degradation of side chain of lignin related aromatic compounds by *Fusarium* spp.
Shojiro Iwahara[*1], Takahito Jomori[*1], Kenji Isshiki[*1], Takayoshi Higuchi[*2]
[*1]Faculty of Agriculture, Kagawa University, [*2]Wood Research Institute, Kyoto University
Keywords: biodegradation, 3,4-dimethoxycinnamaldehyde, 3,4-dimethoxycinnamic acid, pinoresinol, UV spectroscopy

1979-204
リグニンの酸化分解反応（II）. H_2O_2 によるクラフトパルプ廃液の酸化分解処理
辰己憲司[*1]、寺島典二[*2]
[*1] 公害資源研究所、[*2] 名古屋大学農学部
Oxidative degradation of lignin (II), Oxidative degradation treatment of kraft pulp mill effluent with hydrogen peroxide
Kenji Tatsumi[*1], Noritsugu Terashima[*2]
[*1]National Research Institute for Pollution and Resources, [*2]Faculty of Agriculture, Nagoya University
Keywords: *Pinus densiflora*, Fenton reagent, hydroxyl radical, degradation by UV-H_2O_2, COD, TOC

1979-205
クラフト蒸解時のイオウの挙動（VI）蒸解時のメチルメルカプタンについて
近藤隆一郎、近藤民雄
九州大学農学部
Behavior of sulfur during kraft pulping (VI), Methyl mercaptan generated during cooking
Ryuichiro Kondo, Tamio Kondo
Faculty of Agriculture, Kyushu University
Keywords: *Betula Tauschii*, *Pinus densiflora*, volatile organic sulfur, kraft cooking

1979-206
処理木粉によるクラフト臭気成分の吸着処理
池田耕作、近藤隆一郎、近藤民雄
九州大学農学部
Adsorption treatment of kraft smell components with pretreated wood powder
Kosaku Ikeda, Ryuichiro Kondo, Tamio Kondo
Faculty of Agriculture, Kyushu University
Keywords: *Betula Tauschii*, hydrogen sulfide, methyl mercaptan

1979-207
多段オゾン漂白効果の要因について
小林　武、細川　純、久保隆昌、木村　裕
四国工業技術試験所
Factors affecting multistage ozone bleaching
Takeshi Kobayashi, Jun Hosokawa, Takamasa Kubo, Yutaka Kimura
Government Industrial Research Institute, Shikoku
Keywords: ash content, resin content, brightness, viscosity,

1979-208

パルプのオゾン漂白廃水の性状
三浦　清、佐藤礼人
北海道大学農学部
Properties of effluent from ozone bleaching of pulp
Kiyoshi Miura, Ayato Sato
Faculty of Agriculture, Hokkaido University
Keywords: *Betula Tauschii*, kraft pulping, ultrafiltration, UV absorption, BOD, COD

1979-209
針葉樹材 CTMP のオゾン処理
細川　純、久保隆昌、小林　武、赤松　勲
四国工業技術試験所
Ozone treament of softwood CTMP
Jun Hosokawa, Takamasa Kubo, Takeshi Kobayashi, Isao Akamatsu
Government Industrial Research Institute, Shikoku
Keywords: *Pinus densiflora*, sulfur dioxide, folding endurance, breaking length, brightness
1979-210
イピルイピルの SOX 法によるパルプ化
御田昭雄*1、佐伯　剛*2
*1 化学技術研究所, *2 工学院大学
Pulping of *Leucaena leucocephala* by SOX process
Akio Mita*1, Tsuyoshi Saiki*2
*1The Government Chemical Industrial Research Institute, Tokyo, *2Kogakuin University
Keywords: neutral sulfite semichemical pulp, kraft pulp, brightness, ring crush test

1979-211
酸素・アルカリ蒸解の蒸解要因（IV）界面活性剤による脱リグニン促進について
目黒貞利、近藤民雄
九州大学農学部
Cooking factors in oxygen alkali pulping. IV. Promotion of lignin removal by surfactant
Sadatoshi Meguro, Tamio Kondo
Faculty of Agriculture, Kyushu University
Keywords: *Betula Tauschii*, *Pinus densiflora*, sodium laurylbenzene sulfonate, Asplund process, dioxane lignin

1979-212
TMP 法によるパラゴム廃材のパルプ化
久保隆昌、細川　純，小林　武、赤松　勲、小林良生
四国工業技術試験所
Pulping of Para rubber waste wood by TMP process
Takamasa Kubo, Jun Hosokawa, Takeshi Kobayashi, Isao Akamatsu, Yoshio Kobayashi
Government Industrial Research Institute, Shikoku
Keywords: *Hevea brasiliensis*, TMP, freeness, breaking length, tear factor, brightness

1979-213
TMP 法によるバガスパルプの漂白特性
松尾隆吉、西山昌史、小林良生
四国工業技術試験所
Bleaching characteristics of bagasse pulp produced by TMP process
Ryukichi Matsuo, Masashi Nishiyama, Yoshinari Kobayashi
Government Industrial Research Institute, Shikoku
Keywords: sugar cane, *Saccharum* sp, brightness,

1979-214

活性汚泥処におけるクラフトリグニンの挙動
鮫島一彦、高村憲男、瀬戸辰彦
高知大学農学部
Behavior of kraft lignin during treatment with activated sludge
Kazuhiko Sameshima, Norio Takamura, Tatsuhiko Seto
Faculty of Agriculture, Kochi University
Keywords: *Pinus densiflora, Betula Tauschii*, BOD, COD, gel filtration, UV absorption spectroscopy

1979-215
パルプ蒸解廃液からの活性炭製造に関する研究 第4報
戸坂圀夫、鈴木英次、林治助
北海道大学工学部
Studies on the production of activated carbon from pulp waste liquor (IV)
Kunio Tosaka, Eiji Suzuki, Jisuke Hayashi
Faculty of Engineering, Hokkaido University
Keywords: *Abies Mayriana,* steam activation

1979-216
特別講演、リグニン利用の現状と問題点
町原 晃
山陽国策パルプ株式会社
Invited lecture: Present state and problems in utilization of lignin
Akira Machihara
Sanyo-Kokusaku Pulp Co. Ltd.
Keywords: cement dispersant, binder of ore powder, detergent

第25回（1980.10.17-18）九州大学農学部

1980-101
1,2-ジアリールプロパン-1,3–ジオール化合物の *Fusarium solani* による分解
難波宏彰、中坪文明、樋口隆昌
京都大学木材研究所
Degradation of 1,2-diarylpropane-1,3-diol compounds by *Fusarium solani*
Hiroaki Namba, Fumiaki Nakatsubo, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: mass spectrometry, ^{1}H-NMR, UV absorption spectroscopy, phenol oxidase, aldorase

1980-102
シリンギル核を含む β-*O*-4 および β-5 型ジリグノールの *Fusarium solani* による分解
片山健至、中坪文明、樋口隆昌
京都大学木材研究所
Degradation of β-*O*-4 and β-5 dilignols containing syringyl nucleus by *Fusarium solani*
Takeshi Katayama, Fumiaki Nakatsubo, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: biodegradation, syringylglycerol-β-vanillin ether, oxygenase, phenol oxidase

1980-103
Fusarium solani による *d,l*-シリンガレジノールの分解
釜谷保志、中坪文明、樋口隆昌
京都大学木材研究所
Degradation of *d,l*-syringaresinol by *Fusarium solani*
Yasushi Kamaya, Fumiaki Nakatsubo, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: UV absorption spectroscopy, mass spectrometry, ^{1}H-NMR, HPLC, phenol oxidase

1980-104
リグニンの微生物分解に関与する酵素系について
沖　妙、渡部広行、石川久雄
愛媛大学農学部
Enzyme systems participating in microbial degradation of lignin
Tae Oki, Hiroyuki Watanabe, Hisao Ishikawa
Faculty of Agriculture, Ehime University
Keywords: *Lentinus edodes*, *Fagus crenata,* dioxane lignin, guaiacylglycerol-β-guaiacyl ether, UV absorption spectroscopy. gel filtration, phenol oxidase, laccase, peroxidase

1980-105
カタウロコタケ粗酵素によるリグニンの分解（第2報）
—菌体内粗酵素によるミズナラ MWL の分解—
福田　滋、諸星紀幸、原口隆英
東京農工大学農学部
Degradation of lignin by crude enzyme of *Stereum flustulosum* (II), Degradation of Japanese oak MWL by intracellular crude enzyme
Shigeru Fukuda, Noriyuki Morohoshi, Takafusa Haraguchi
Faculty of Agriculture, Tokyo University of Agriculture and Technology
Keywords: syringic acid, 2,6-dimethoxy-1,4-benzoquinone, IR spectrum

1980-106
リグニン生分解と酸化還元酵素
石原達夫
林業試験場

Biodegradation of lignin and oxidoreductase
Tatsuo Ishihara
Forestry and Forest Products Research Institute
Keywords: *Pleurotus ostreatus*, *Betula Tauschii*, laccase, cellobiose oxidase, redox potential,

1980-107
木材腐朽菌（カワラタケ）によるリグニンモデル化合物の代謝
片山義博
筑波大学農林工学系
Metabolism of lignin model compounds by wood rotting fungi *Coridus versicolor*
Yoshihiro Katayama
Institute of Agricultural and Forest Engineering, University of Tsukuba
Keywords: syringaresinol, pinoresinol, UV absorption spectroscopy, ^{1}H-NMR, ^{13}C-NMR,

1980-108
Phanerochaete chrysosporium によるフェニルクマラン型二量体の分解機構の研究
梅澤俊明[*1]、中坪文明[*1]、樋口隆昌[*1]、T.K. Kirk[*2]
[*1] 京都大学木材研究所、[*2]マジソン林産物研究所
Degradation mechanism of phenylcoumaran type dimer by *Phanerochaete chrysosporium*
Toshiaki Umezawa[*1], Fumiaki Nakatsubo[*1], Takayoshi Higuchi[*1], T.K. Kirk[*2]
[*1]Wood Research Institute, Kyoto University, [*2] Forest Products Laboratory, Madison, U.S.A
Keywords: 2-(4-hydroxy-3,5-dimethoxyphenyl)-3-hydroxymethyl-5-formyl-7-methoxycoumaran, phenol oxidase

1980-109
硫酸リグニンの化学構造
—アリールグリセロール-β-アリールエーテル型構造からの縮合物の化学構造—
安田征市、寺島典二、伊東　健
名古屋大学農学部
Chemical structures of sulfuric acid lignin, —Chemical structures of condensation products from arylglycerol-β-aryl ether type structures—
Seiichi Yasuda, Noritsugu Terashima, Takeshi Ito
Faculty of Agriculture, Nagoya University
Keywords: ^{13}C-NMR, creosol, phenylcoumaran, Hibbert's ketone, diphenylpropane compounds

1980-110
木酢液について
黒田健一
筑波大学農林工学系
On the wood vinegar
Kenichi Kuroda
Institute of Agricultural and Forest Engineering, University of Tsukuba
Keywords: *Pinus densiflora,* dioxane lignin, nitrobenzene oxidation, permanganate oxidation, HPLC, guaiacol, creosol, 4-ethylguaiacol

1980-111
カキシブの硬化機構
田中治郎
林業試験場
Hardening mechanism of persimmon juice
Jiro Tanaka
Forestry and Forest Products Research Institute
Keywords: UV spectroscopy, IR spectroscopy, carbonyl group

1980-112
ビーズ状リグニン樹脂の製造に関する研究
飯塚堯介、中野準三
東京大学農学部
Studies on production of beads type resin from lignin
Gyosuke Meshitsuka, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: hardwood lignosulfonic acid, two-step resinification, one-step resinification

1980-113
リグニンの酸化分解（III） —H_2O_2によるリグニンモデル化合物の酸化分解—
辰己憲司[*1]、寺島典二[*2]
[*1] 公害資源研究所、[*2] 名古屋大学農学部
Oxidative degradation of lignin (III), Oxidative degradation of lignin model compounds with hydrogen peroxide
Kenji Tatsumi[*1], Noritsugu Terashima[*2]
[*1]National Research Institute for Pollution and Resources, [*2]Faculty of Agriculture, Nagoya University
Keywords: UV radiation, pH dependence, veratric acid, vanillic acid, protocatechuic acid

1980-114
リグニンのオゾン分解について
金子英信、中野準三
東京大学農学部
Degradation of lignin with ozone
Hidenobu Kaneko, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: lignin model compound, thiolignin, surface tension, dispersion effect, dispersion number, ^{1}H-NMR, ^{13}C-NMR,

1980-115
クラフト蒸解廃液中の生物活性物質
重松章彦、鮫島一彦、高村憲男
高知大学農学部
Bioactive substances in kraft pulp waste liquor
Akihiko Shigematsu, Kazuhiko Sameshima, Norio Takamura
Faculty of Agriculture, Kochi University
Keywords: *Pinus densiflora, Betula Tauschii*, *Oryzias latipes,* medaka bioassay, toxicity,

1980-116
パルプ廃液中の有機塩素化合物の毒性および分解性
島田謹爾
林業試験場
Toxicity and degradability of organic chlorine compounds in pulp waste liquor
Kinji Shimada
Forestry and Forest Products Research Institute
Keywords: bioassay, *Oryzias latipes,* trichloroguaiacol, trichlorosyringol

1980-117
特別講演、石炭の液化と炭化
竹下健次郎
九州大学生産科学研究所
Invited lecture: Liquefaction and carbonization of coal
Kenjiro Takeshita
Kyushu University Research Institute for Production Science
Keywords: model compounds of coal, coal pitch, mesophase, microphotograph

1980-201
不斉場におけるコニフェリルアルコールの脱水素重合
三木啓司、榊原　彰
北海道大学農学部
Dehydrogenative polymerization of coniferyl alcohol in chiral environment
Keiji Miki, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords:　*Quercus mongolica*, *Larix leptorepis*, holocellulose, hemicellulose, gel filtration

1980-202
シナポイル CoA リガーゼの植物間分布及び性質について
久津木英俊、島田幹夫、樋口隆昌
京都大学木材研究所
Occurrence of synapoyl Co-A ligase among plants and its properties
Hidetoshi Kutsuki, Mikio Shimada, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords:　*Erythrina crista-galli*, feruloyl Co-A ligase, 5-hydroxyferulic acid

1980-203
広葉樹プロトリグニンの水素化分解物に関する研究
黄　炳浩、榊原　彰
北海道大学農学部
Studies on the hydrogenolysis products from hardwood protolignin
Byung Ho Hwang, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords:　*Fraxinus mandshurica var. japonica,* mass spectrometry, ^{1}H-NMR, diarylpropane derivative

1980-204
カラマツアテ材リグニンの水素化分解に関する研究
小林千益、安田征市、榊原　彰
北海道大学農学部
Studies on the hydrogenolysis of lignin in compression wood of larch
Seneki Kobayashi, Seiichi Yasuda, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords:　*Larix leptolepis*, phenylisochromane, diarylpropane, lignaloid, lappaol A,B,C,D

1980-205
アリールグリセロール-β-アリールエーテル型構造の選択的解裂について
松本雄二、石津　敦、中野準三
東京大学農学部
Selective cleavage of arylglycerol-β-aryl ether type structure
Yuji Matsumoto, Atsushi Ishizu, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords:　*Picea jezoensis*, γ-*p*-toluenesulfinyl veratrylglycerol-β-guaiacyl ether, MWL, gel filtration

1980-206
エゾマツブラウンズリグニン（BL）の性質について
高橋秀敏、青山政和、榊原　彰
北海道大学農学部
On the properties of Brauns's lignin (BL) from Yezo spruce
Hidetoshi Takahashi, Masakazu Aoyama, Akira Sakakibara
Faculty of Agriculture, Hokkaido University

Keywords: *Picea jezoensis*, lignan, western hemlock, *Tsuga heterophylla*, ^{1}H-NMR, ^{13}C-NMR

1980-207
磨砕時間を異にして段階的に単離した広葉樹 MWL の性状について
李　忠正、飯塚堯介、中野準三
東京大学農学
Characteristics of hardwood MWL isolated with different milling times
Zhong Zheng Lee, Gyosuke Meshitsuka, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: birch, *Betula* sp., cell wall layers, nitrobenzene oxidation, non-conjugated phenolic hydroxyl group,

1980-208
ヘミセルロース・リグニン結合体に関する研究（その 4）—アカマツあて材 MWL 画分よりのヘミセルロース・リグニン結合体の性質
向吉俊一郎、東　順一、越島哲夫
京都大学木材研究所
Studies on the hemicellulose-lignin complex (IV), Characteristics of hemicellulose-lignin complex obtained from MWL fraction of red pine compression wood
Shunichiro Mukoyoshi, Junichi Azuma, Tetsuo Koshijima
Wood Research Institute, Kyoto University
Keywords: *Pinus densiflora*, gel filtration, methylation analysis, Smith degradation, galactose

1980-209
ユーカリ材チップの劣化
岡山隆之、蔵本　敬、屋部雅夫、大江礼三郎
東京農工大学農学部
Biodegradation of eucalyptus wood chip
Takayuki Okayama, Takashi Kuramoto, Masao Yabe, Raysabro Oye
Faculty of Agriculture, Tokyo University of Agriculture and Technology
Keywords: thermal degradation, Klason lignin, holocellulose

1980-210
硝酸法蒸解におけるリグニンの挙動について　—モデル実験—
Huynh Van Ba、石津　敦、中野準三
東京大学農学部
Behavior of lignin during nitric acid pulping, —Model experiments—
Huynh Van Ba, Atsushi Ishizu, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: apocynol, guaiacylglycerol-β-guaiacyl ether, veratrylglycerol-β-guaiacyl ether, TLC

1980-211
クラフト蒸解における木材成分の溶出挙動と黒液成分の変化
玉生征人，炭村栄一，高橋　武，上埜武夫
山陽国策パルプ株式会社
Dissolution of wood components and change of black liquor composition during kraft cooking
Masato Tamao, Eiichi Sumimura, Takeshi Takahashi, Takeo Ueno
Sanyo Kokusaku Pulp Co., Ltd.
Keywords: lignin, carbohydrate, low molecular fraction, high molecular fraction, active alkali,

1980-212
バガスの過酸化水素アルカリ蒸解について
御田昭雄、柏原　進、河村英司
化学技術研究所
Pulping of bagasse with hydogenperoxide and alkali

Akio Mita, Susumu Kashiwabara, Eishi Kawamura
The Government Chemical Industrial Research Institute, Tokyo
Keywords: energy consumption, pulp yield, Kappa number, pentosan content

1980-213
KP の酸素-オゾン-過酸化水素漂白
藤井利郎、上嶋 洋、赤松 勲
四国工業技術試験所
Bleaching of KP with oxygen-ozone-hydrogen peroxide
Toshiro Fujii, Hiroshi Kamishima, Isao Akamatsu
Government Industrial Research Institute, Shikoku
Keywords: *Pseudotsuga taxifolia*, viscosity, brightness

1980-214
パルプのオゾン漂白に関する研究
三浦 清、香山 彊
北海道大学農学部
Studies on the ozone bleaching of pulp
Kiyoshi Miura, Tsutomu Kayama
Faculty of Agriculture, Hokkaido University
Keywords: *Abies Mayriana*, SEM (scanning electron microscopy), ESR (electron spin resonance spectroscopy)

1980-215
薬液添加TMPの製造とその品質について
加地隆男，菊池春朗，河村道雄
大王製紙株式会社
Manufacturing and properties of TMP with chemicals
Takao Kaji, Shunro Kikuchi, Michio Kawamura
Daio Paper Corporation
Keywords: *Picea* sp., *Eucalyptus,* high yield pulp, resource saving, specific energy consumption, domestic pine,

1980-216
針葉樹 CTMP に関する研究 —収率差における物性と漂白性について—
小島康夫、香山 彊
北海道大学農学部
Studies on the softwood CTMP. —Relation between pulp yield and physical properties, and bleachability

Yasuo Kojima, Tsutomu Kayama
Faculty of Agriculture, Hokkaido University
Keywords: *Picea Glehnii,* freeness, density, printing opasity, brightness,

1980-217
総合討論、これからのリグニン研究 —若手研究者の立場から—
飯山賢治（東京大学農学部 司会）、安田征市（名古屋大学農学部）、鮫島一彦（高知大学農学部）、飯塚堯介（東京大学農学部）、中坪文明（京都大学木質科学研究所）
General discussion on “Future prospects of lignin research”, From young researchers
Moderator: Kenji Iiyama (Faculty of Agriculture, the University of Tokyo)
Seiichi Yasuda (Faculty of Agriculture, Nagoya University)
Kazuhiko Sameshima (Faculty of Agriculture, Kochi University)
Gyosuke Meshitsuka (Faculty of Agriculture, the University of Tokyo)
Fumiaki Nakatsubo (Faculty of Agriculture, Kyoto University)

第26回（1981.10.29-30）工業技術院筑波研究センター

1981-101
Fusarium solani によるグリセロール−2−バニリン酸エーテルおよびフェニルクマラン型二量体の分解
片山健至、中坪文明、樋口隆昌
京都大学木材研究所
Degradation of glycerol-2-vanilic acid ether and phenylcoumaran-type dimer by *Fusarium solani*
Takeshi Katayama, Fumiaki Nakatubo, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: biodegradation, *Fusarium solani* , arylglycerol-β-aryl ether, phenylcoumaran

1981-102
Fusarium solani による *d,l*-シリンガレジノールの分解（その 2）
釜谷保志、中坪文明、樋口隆昌
京都大学木材研究所
Degradation of *d,l*-syringaresinol by *Fusarium solani*, II.
Yasushi Kamaya, Fumiaki Nakatsubo, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: biodegradation, *Fusarium solani*, syringaresinol

1981-103
カワラタケ・ラッカーゼの分別と精製及び 2，3 の性質
村磯知採、割石博之、永井 享、諸星紀幸、原口隆英
東京農工大学農学部
Fractionation and purification of laccase from *Coriolus versicolor* and its properties
Chidori Muraiso, Hiroyuki Wariishi, Tooru Nagai, Noriyuki Morohoshi, Takafusa Haraguchi
Faculty of Agriculture, Tokyo University of Agriculture and Technology
Keywords: Laccase, *Coriolus versicolor*

1981-104
カワラタケ・ラッカーゼによるリグニンの変化（第 2 報）−BNL，MWL，LCC，残渣木粉中のリグニンの定量的変化量について−
諸星紀幸、原口隆英
東京農工大学農学部
Changes of lignin by laccase from *Coriolus versicolor* (II), Quantitative evaluation of changes of lignin in BNL, MWL, LCC, residual wood meal
Noriyuki Morohoshi, Takafusa Haraguchi
Faculty of Agriculture, Tokyo University of Agriculture and Technology
Keywords: laccase, *Coriolus versicolor*

1981-105
Lentinus edodes 体外酵素による guaiacylglycerol-β-guaiacyl ether の分解
沖 妙、仙波裕子、石川久雄
愛媛大学農学部
Degradation of guaiacylglycerol-β-guaiacyl ether by the extracellular enzyme of *Lentinus edodes*
Tae Oki, Yuko Sennami, Hisao Ishikawa
Faculty of Agriculture, Ehime University
Keywords: *Lentinus edodes*, guaiacylglycerol-β-guaiacyl ether

1981-106
Phanerochaete chrysosporium によるフェノール性水酸基をもつフェニルクマラン型二量体の分解
梅澤俊明、中坪文明、樋口隆昌
京都大学木材研究所
Degradation of a phenolic phenylcoumaran-type dimer by *Phanerochaete chrysosporium*

Toshiaki Umezawa, Fumiaki Nakatsubo, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: phenylcoumaran, dimer, *Phanerochaete chrysosporium*

1981-107
担子菌の変異株を用いたベラトリルアルコール代謝とリグニンの『生合成』的生分解に関する研究
島田幹夫[*1]、樋口隆昌[*1]、M.H. Gold[*2]
[*1] 京都大学木材研究所、[*2]OGC
Studies on the metabolism of veratrylalcohol by the mutant of basidiomycete and the biosynthetic degradation of lignin
Mikio Shimada[*1], Takayoshi Higuchi[*1], M.H. Gold[*2]
[*1]Wood Ressearch Institute , Kyoto University, [*2]Oregon Graduate Center
Keywords: Biosynthetic degradation, mutant, basidiomycetes, veratryl alcohol

1981-108
キノンメチド中間体を経る LCC モデルの形成に関する研究
棚橋光彦、樋口隆昌
京都大学木材研究所
Studies on the formation of LCC model compounds through quinone methide intermediate
Mitsuhiko Tanahashi, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: LCC model, quinine methide, glucose, xylose

1981-109
リグニンの KMnO4 酸化分解
佐野嘉拓[*1]、W.G. Glasser[*2]
北海道大学農学部
Oxidative degradation of lignin with KMnO4
Yoshihiro Sano[*1], W.G.Glasser[*2]
[*1]Faculty of Agriculture, Hokkaido University, [*2]Virginia Polytechnic Institute and State University
Keywords: $KMnO_4$ oxidation, MWL

1981-110
オゾノリシスによるリグニン中の glyceraldehyde−2−aryl ether 構造の定量
松本雄二、石津　敦、中野準三
東京大学農学部
Quantitative determination of glyceraldehyde-2-aryl ether in lignin by ozonolysis
Yuji Matsumoto, Atsushi Ishizu, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: glyceraldehydes-2-aryl ether, ozonolysis, glycerol

1981-111
広葉樹プロトリグニンの水素化分解物に関する研究　—新 2 量体の単離—
黄　柄浩、榊原　彰
北海道大学農学部
Hydrogenolysis of hardwood protolignin, -Isolation of a new dimer
Byung Ho Hwang, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: hydrogenolysis, hardwood lignin, new dimer

1981-112
クラフトパルプ中の残留リグニンの性状
山崎　岳、細谷修二、Chen C. L., Gratzl J.S., Chang H.-m.
ノースカロライナ州立大学

Properties of residual lignin in kraft pulp
Takeshi Yamasaki, Shuji Hosoya, C. L. Chen, J.S. Gratzl, H.-m. Chang
North Carolina State University
Keywords: residual lignin, kraft pulp, enzymatic treatment, lignin-carbohydrate linkage in pulp

1981-113
硫酸リグニンの化学構造　―アリールグリセロール-β-アリールエーテルと 72%硫酸との反応―
安田征市、寺島典二、伊東　健
名古屋大学農学部
Structures of sulfuric acid lignin,-Reactions of arylglycerol-β-aryl ether in 72% sulfuric acid
Seiichi Yasuda, Noritsugu Terashima, Takeshi Ito
Faculty of Agriculture, Nagoya University
Keywords: sulfuric acid lignin, arylglycerol-β-ary ether, acid condensation

1981-114
水分及び熱処理によるリグニン主分散の変化
矢野彰一郎、品川俊一、畠山兵衛
製品科学研究所
Changes in the main dispersion of dynamic viscoelasticity curves of lignin by water and heat treatment
Shoichiro Yano, Shunichi Shinagawa, Hyoe Hatakeyama
Industrial Products Research Institute
Keywords: Tg, polystyrene, dynamic viscoelasticity

1981-115
ヘミセルロース・リグニン結合体（LCC）に関する研究（その 5）−アカマツ圧縮アテ材よりの Björkman LCC の性質―
東　順一[*1]、向吉俊一郎[*1*2]、越島哲夫[*1]
[*1] 京都大学木材研究所, [*2] 神崎製紙株式会社
Studies on lignin hemicellulose complex (LCC) (V), Characterization of Björkman LCC from red pine compression wood
Junichi Azuma[*1], Shunichiro Mukoyoshi [*1*2], Tetsuo Koshijima[*1]
[*1]Wood Research Institute, Kyoto University; [*2]Kanzaki Paper Co. Ltd.
Keywords: *Pinus densiflora,* hemicellulose, GPC

1981-116
リグニン―糖結合体の性状について
飯塚堯介[*1]、李　忠正[*1]、中野準三[*1]、江田　茂[*2]
[*1] 東京大学農学部、[*2] 日本専売公社中央研究所
Characterization of lignin-carbohydrate complex
Gyosuke Meshitsuka[*1], Zhong Zheng Lee [*1], Junzo Nakano[*1], Shigeru Eda[*2]
[*1]Faculty of Agriculture, the University of Tokyo, [*2] Central Research Institute, Japan Tobacco and Salt Public Corporation
Keywords: LCC, pectinase, GPC

1981-117
特別講演、C_1 化学について
阪東憲一郎
化学技術研究所
Invited Lecture ; C-1 Chemistry
Kenichiro Bando
National Chemical Laboratory for Industry

1981-201
亜塩素酸塩法及び過酢酸法によるホロセルロースの調製過程で溶出する多糖成分について

前川英一、越島哲夫
京都大学木材研究所
Dissolution of polysaccharides during the hollocellulose preparation with sodium chlorite and peracetic acid methods
Eiichi Maekawa, Tetsuo Koshijima
Wood Research Institute, Kyoto University
Keywords: *Pinus densiflora, Fagus crenata*, degree of delignification, UV absorption spectroscopy

1981-202
高収率パルプを用いるカルボキシメチルセルロースの調製（II) —カルボキシメチル化リグニンの加熱処理に対する挙動—
ラム・チ・バック・チュエット、石津　敦、中野準三
東京大学農学部
Preparation of carboxymethyl cellulose from high-yield pulp (II), Behavior of carboxymethyl lignin on heating
Thi Bach Tuyet Lam, Atsushi Ishizu, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: *Picea jezoensis,* MWL, carboxymethyl cellulose, high-yield pulp, carboxymethyl lignin

1981-203
リグニン存在下でのセルロース質の酵素分解
夜久富美子[*1]、田中龍太郎[*1]、村木永之介[*1]、足立公洋[*1]、越島哲夫[*2]
[*1] 大阪工業技術試験所、[*2] 京都大学木材研究所
Enzymatic hydrolysis of cellulosic materials in the presence of lignin
Fumiko Yaku[*1], Ryutaro Tanaka[*1], Einosuke Muraki[*1], Kimihiro Adachi[*1], Tetsuo Koshijima[*2]
[*1]Government Industrial Research Institute, Osaka, [*2]Wood Research Institute, Kyoto University
Keywords: *Pinus densiflora,* vibration ball mill, roll mill, cellulase

1981-204
リグニンおよび関連物質の熱分解（第 1 報）
佐々木坤彪、鈴木正人、佐方克彦、長沢武夫
日本紙パルプ研究所
Pyrolysis of lignin and related materials (I)
Nobutake Sasaki, Masato Suzuki, Katsuhiko Sakata, Takeo Nagasawa
Japan Pulp ＆ Paper Research Institute, Inc.
Keywords: *Fagus crenata*, chlorinated compound, chlorinated lignin

1981-205
4−n−アルコキシ−3−メトキシ安息香酸誘導体の液晶性
春日和行、畠山兵衛
製品科学研究所
Properties of 4-n-alkoxy-3-methoxybenzoic acid derivatives as liquid crystal
Kazuyuki Kasuga, Hyoe Hatakeyama
Industrial Products Research Institute
Keywords: vanillin, alkyl chain length, transition temperature,

1981-206
リグニンの酸化分解（IV）紫外線照射下での H_2O_2 とリグニンモデル化合物の芳香核との反応
辰巳憲司[*1]、寺島典二[*1]
[*1] 公害資源研究所、[*2] 名古屋大学農学部
Oxidative degradation of lignin (IV), Reactions of aromatic rings of lignin model compounds with hydrogen peroxide under UV irradiation
Kenji Tatsumi[*1], Noritsugu Terashima[*2]
[*1]National Research Institute for Pollution and Resources, [*2]Faculty of Agriculture, Nagoya University
Keywords: HPLC, vanillic acid, protocatechuic acid

1981-207
木材の液化に関する研究 (I) —アルカリ-アルコール法による樹皮の液化—
須藤賢一
林業試験場
Liquefaction of wood (I), -Liquefaction of bark by alkali-alcohol system
Kenichi Sudo
Forestry and Forest Products Research Institute
Keywords: GPC, IR absorption spectroscopy, ^{1}H-NMR

1981-208
水素化によるパルプ製造に関する研究
榊原 彰、枝重有祐、植松敏夫、武山浩武
北海道大学農学部
Hydrogenolysis pulping
Akira Sakakibara, Yusuke Edasige, Toshio Uematsu, Hirotake Takeyama
Faculty of Agriculture, Hokkaido University
Keywords: *Betula platyphylla,* phenol, cresols, xylenols, guaiacol

1981-209
高収率パルプに関する研究 —化学前処理とリファイニングエネルギー—
坂井克己
九州大学農学部
Studies on high yield pulp. -Chemical pretreatment and refining energy
Kokki Sakai
Faculty of Agriculture, Kyushu University
Keywords: *Pinus Thunbergii,* sodium sulfite, sodium chlorite, refining energy

1981-210
CMP のリファイニング条件について
大森隆志、坂井克己
九州大学農学部
Refining conditions of chemi-mechanical pulp
Takashi Ohmori, Kokki Sakai
Faculty of Agriculture, Kyushu University
Keywords: CGP, RGP, TMP, sodium sulfite

1981-211
ジャイアント・レウカエナ材の CTMP 法による新聞紙級パルプ
久保隆昌[*1] 細川 純[*1]、小林 武[*1]、赤松 勲[*1]、小林良生[*1]、Supasuri Janesuthiwechakul[*2]
四国工業技術試験所
Production of newspaper grade CTMP from giant leucaena
Takamasa Kubo[*1], Jun Hosokawa[*1], Takeshi Kobayashi[*1], Isao Akamatsu[*1], Yoshinari Kobayashi[*1], Supasri Janesuthiwechakul[*2]
[*1]Government Industrial Research Institute, Sikoku, [*2]Royal Forest Dept. Thailand
Keywords: giant leucaena, *Leucaena glauca,* sodium sulfite, pulp properties, refining energy

1981-212
高歩留パルプの改質 —ラジカル的スルホン化反応による TMP の改質—
大井 洋、飯塚堯介、中野準三
東京大学農学部
Improvement of high yield pulp.-Improvement of TMP by radical sulfonation
Hiroshi Ohi, Gyosuke Meshitsuka, Junzo Nakano
Faculty of Agriculture, the University of Tokyo

Keywords: *Picea jezoensis,* sodium sulfite, potassium permanganate, manganese dioxide,

1981-213
木材チップの圧縮と蒸解性
岡山隆之、木下卓麻、大江礼三郎
東京農工大学農学部
Effect of roll-pressing of wood chips on pulping
Takayuki Okayama, Takuma Kinoshita, Reisabro Oye
Faculty of Agriculture, Tokyo University of Agriculture and Technology
Keywords: *Eucalyptus marginata*, *Pinus densiflora,* roll pressing, shear, kraft pulping

1981-214
ネマガリダケのパルプ化に関する研究
戸坂圀夫[*1]、望月　明[*1]、林　治助[*1]、ヌエ・ニイ・ウェイ[*2]
[*1] 北海道大学工学部、[*2] 京都大学農学部
Studies on pulping of *Sasa kurilensis*
Kunio Tosaka[*1], Akira Mochizuki[*1], Jisuke Hayashi[*1], *????????[*2]
[*1]Faculty of Engineering, Hokkaido University, [*2]Faculty of Agriculture, Kyoto University
Keywords: *Sasa kurilensis*, kraft pulping, soda pulping, oxygen alkali pulping

1981-2015
酸素・アルカリ蒸解の蒸解要因　—グアヤコールの酸素酸化に及ぼす酸素担体添加の効果−
目黒貞利
九州大学農学部
Factors influencing oxygen-alkali cooking, -Effects of oxygen carrier on the oxidation of guaiacol
Sadatoshi Meguro
Faculty of Agriculture, Kyushu University
Keywords: oxygen carrier, Co-salen, Co-salpr

1981-2016
シュウ酸添加オゾン漂白におけるシュウ酸の回収と再使用
藤井利郎、上嶋　洋、赤松　勲
四国工業技術試験所
Recovery and reuse of oxalic acid from effluent of ozone bleaching with oxalic acid
Toshio Fujii, Hiroshi Kamishima, Isao Akamatsu
Government Industrial Research Institute, Shikoku
Keywords: *Pseudotsuga taxifolia,* cellulose protectant, calcium oxalate

1981-2017
特別講演、今後のリグニン化学工業の展望
秦　邦男
十條製紙株式会社中央研究所
Invited lecture ; Future prospects of industrial utilization of lignin
Kunio Hata
Central Research Institute, Jujo Paper Co. Ltd.

第 27 回（1982.10.21-22）名古屋大学農学部

1982-101
オゾノリシスを用いたリグニン側鎖構造の研究 —各種単離リグニンへの適用—
松本雄二、石津　敦、中野準三
東京大学農学部
Studies on the structure of lignin side chain by ozonolysis,-Application to various isolated lignins
Yuji Matsumoto, Atsushi Ishizu, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: *Picea jezoensis*, MWL, erythronic acid, threonic acid, glyceraldehydes-2-aryl ether, ^{13}C-NMR

1982-102
針葉樹リグニンへのシリンギル核の導入
飯山賢治、R. Pant、中野準三
東京大学農学部
Introduction of syringyl nuclei to softwood lignin
Kenji Iiyama, R. Pant, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: *Picea jezoensis*, *Fagus crenata,* MWL, Mäule color reaction, Fremy's salt oxidation

1982-103
スギ心材の色とリグニン
黒田宏之、島地　謙
京都大学木材研究所
Color and lignin of Japanese cedar heartwood
Hiroyuki Kuroda, Ken Shimaji
Wood Research Institute, Kyoto University
Keywords: Japanese cedar, *Cryptomeria japonica,* MWL, LCC, microspectroscopy, morphology

1982-104
逐次アシドリシスにより溶出するリグニンの分子構造
船岡正光、阿部　勲
三重大学農学部
Structure of lignin dissolved by stepwise acidolysis
Masamitsu Funaoka, Isao Abe
Faculty of Agriculture, Mie University
Keywords: condensed structure, nuclear exchange reaction, nitrobenzene oxidation

1982-105
リグニンおよびリグニン関連型ポリスチレン誘導体の水素結合と吸着水
畠山兵衛[*1]、広瀬重雄[*1]、中村邦雄[*2]、畠山立子[*3]
[*1] 製品科学研究所、[*2] 神奈川県工業試験所，[*3] 繊維高分子材料研究所
Hydrogen bond and adsorbed water of lignin and lignin-like polystyrene derivatives
Hyoe Hatakeyama[*1], Shigeo Hirose[*1], Kunio Nakamura[*2], Tatsuko Hatakeyama[*3]
[*1]Industrial Products Research Institute, [*2]Kanagawa Industrial Technology Center, [*3]Research Institute for Polymers and Textiles
Keywords: *Libocedrus decurrens,* dioxane lignin, lignin-like polystyrene derivatives, thermal analysis, glass transition temperature

1982-106
リグニン—糖間結合に対するペクチン質の寄与
飯塚堯介、中野準三
東京大学農学部
Contribution of pectic substances to lignin carbohydrate bond

Gyosuke Meshitsuka, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: birch, *Betula* sp., endo-pectin lyase, endo-polygalacturonase, pectin esterase, LCC

1982-107
リファイナーメカニカルパルプを用いるカルボキシメチルセルロースの調製（第 3 報）カルボキシメチル化炭水化物の溶出に及ぼすリグニンの影響
ラム・チ・バック・チュエット、飯山賢治、石津 敦、中野準三
東京大学農学部
Preparation of carboxymethyl cellulose from refiner mechanical pulp (III), Effect of lignin on the dissolution of carboxymethylated carbohydrates
Thi Bach Tuyet Lam, Kenji Iiyama, Atsushi Ishizu, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: *Picea jezoensis, Fagus crenata,* mannan, xylan, ^{1}H-NMR,

1982-108
針葉樹仮道管の壁形成における多糖類とリグニンの堆積
高部圭司、藤田 稔、佐伯 浩、原田 浩
京都大学農学部
Deposition of polysaccharides and lignin during the cell wall formation of softwood tracheids
Keiji Takabe, Minoru Fujita, Hiroshi Saiki, Hiroshi Harada
Faculty of Agriculture, Kyoto University
Keywords: *Cryptomeria japonica,* UV microscopy, autoradiography, ^{3}H-glucose, ^{14}C-glucose, ^{3}H-phenylalanine

1982-109
アカマツ圧縮アテ材の脱リグニン液中に溶出してくる多糖の性質
東 順一[*1]、向吉俊一郎[*1][*2]、越島哲夫[*1]
[*1] 京都大学木材研究所、[*2] 神崎製紙株式会社
Characterization of polysaccharides dissolving out during the delignification of red pine compression wood
Junichi Azuma[*1], Mukoyoshi Shunichiro[*1][*2], Tetsuo Koshijima[*2]
[*1]Wood Research Institute, Kyoto University, [*2]Kanzaki Paper Co. Ltd.
Keywords: *Pinus densiflora*, LCC, sodium chlorite, galactoglucomannan

1982-110
リグニンの酸化分解（V）酸素およびヒドロキシラジカルとリグニンの芳香核との反応
辰己憲司[*1]、寺島典二[*2]
[*1] 公害資源研究所、[*2] 名古屋大学農学部
Oxidative degradation of lignin (V), Reactions of lignin aromatic nuclei with oxygen and hydroxyl radical
Kenji Tatsumi[*1], Noritsugu Terashima[*2]
[*1] National Research Institute for Pollution and Resources, [*2]Faculty of Agriculture, Nagoya University
Keywords: UV radiation, pH dependence, vanillic acid, protocatechuic acid, gallic acid

1982-111
求核性試薬添加ソーダ蒸解
大原誠資、飯塚堯介、R. Pant、中野準三
東京大学農学部
Soda pulping with addition of nucleophilic reagents
Seiji Ohara, Gyosuke Meshitsuka, R. Pant, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: soda pulping, nucleophilic reagent, methyl mercaptan, thiophenol

1982-112
酸素・アルカリ蒸解の蒸解要因。 Co-Salen 触媒活性に及ばす蒸解因子の影響

目黒貞利、今村博之
九州大学農学部
Cooking factors influencing oxygen-alkali pulping. -Factors influencing the catalytic activity of Co-salen
Sadatoshi Meguro, Hiroyuki Imamura
Faculty of Agriculture, Kyushu University
Keywords: cobalt (II) bis(salicylidene)ethylenediamine, oxidation of guaiacol,

1982-113
クレゾール・水によるパルプ化法について
榊原 彰、技重有祐、武山浩武
北海道大学農学部
Pulping with cresol and water
Akira Sakakibara, Yusuke Edashige, Hirotake Takeyama
Faculty of Agriculture, Hokkaido University
Keywords: *Picea Glehnii,* organosolv pulping,

1982-114
オルガノソルブパルプ化に関する研究
佐野嘉拓、榊原 彰、笹谷宜志
北海道大学農学部
Studies on organosolv pulping
Yoshihiro Sano, Akira Sakakibara, Takashi Sasaya
Faculty of Agriculture,Hokkaido University
Keywords: *Quercus crispula, Betula Tauschii*, *Picea Glehnii, Larix Kaempferi, Abies Mayriana,* phenol, cresol,

1982-115
有機溶媒とサルファイトによるパルプ化（I） スギSCP蒸解におけるイソプロピルアルコール添加の効果（その1）
文 星筆、坂井克己、今村博之
九州大学農学部
Pulping with organic solvents and sulfite (I), Effects of the addition of isopropyl alcohol on SCP cooking of Japanese cedar
Sung-Phil Mun, Kokki Sakai, Hiroyuki Imamura
Faculty of Agriculture, Kyushu University
Keywords: *Cryptomeria japonica,* neutral sulfite, monosulfite, bisulfite, isopropyl alcohol, Japanese cedar

1982-116
広葉樹（GL材）CTMPの強度と繊維特性
久保隆昌、細川 純、小林 武、赤松 勲
四国工業技術試験所
Strength properties and fiber characteristics of hardwood CTMP
Government Industrial Research Institute, Shikoku
Takamasa Kubo, Jun Hosokawa, Takeshi Kobayashi, Isao Akamatsu
Keywords: giant leucaena, *Leucaena leucocephala*, TMP,

1982-117
リグニンおよび関連物質の熱分解（第3報）
佐々木坤彪、荒木 廣、鈴木正人、長沢武夫
日本紙パルプ研究所
Pyrolysis of lignin and related materials (III)
Nobutake Sasaki, Hiroshi Araki, Masato Suzuki, Takeo Nagasawa
Japan Pulp & Paper Research Institute, Inc.

Keywords: *Fagus crenata*, thiolignin, pyrolysis, chlorinated lignin, TG, DSC

1982-118
特別講演、木材の細胞壁の構造と形成
原田　浩
京都大学農学部
Invited lecture ; Structure and formation of wood cell wall
Hiroshi Harada
Faculty of Agriculture, Kyoto University
Keywords: vascular cambium, chemical composition, cell wall layers

1982-201
大気汚染地域で見られたスギ葉中のタンニン生合成阻害について
加藤輝隆[*1]、加須屋実[*1]、鏡森定信[*1]、河野昭一[*2]
富山医科薬科大学医学部、富山大学生物学科
Inhibition of tannin biosynthesis in the leaves of Japanese cedar in the air pollutied area
Terutaka Kato[*1], Minoru Kasuya[*1], Sadanobu Kagamimori[*1], Shoichi Kawano[*2]
[*1]Faculty of Medicine, Toyama Medical and Pharmaceutical University, [*2]Department of Biology, Toyama University
Keywords: *Cryptomeria japonica,* glucose content, shikimic acid

1982-202
リグニン存在下でのセルロース質の酵素分解（2）
夜久富美子[*1]、田中龍太郎[*1]、村木永之介[*1]、田中文男[*2]、越島哲夫[*2]
[*1] 大阪工業技術試験所、[*2] 京都大学木材研究所
Enzymatic hydrolysis of cellulosic substance in the presence of lignin (II)
Fumiko Yaku[*1], Ryutaro Tanaka[*1], Einosuke Muraki[*1], Fumio Tanaka[*2], Tetsuo Koshijima[*2]
[*1]Government Industrial Research Institute, Osaka, [*2]Wood Research Institute, Kyoto University
Keywords: *Pinus densiflora, Shorea negrosensis*, *Pentacme contorta*, vibration ball mill, MWL, LCC,

1982-203
爆砕木材の特性とその酵素糖化
棚橋光彦[*1]、樋口隆昌[*1]、高田信輔[*2]、花井四郎[*3]
[*1] 京都大学木材研究所、[*2] 近畿大学農学部、[*3] 宝酒造株式会社
Characterization of steam-exploded wood and its enzymatic hydrolysis
Mitsuhiko Tanahashi, Takayoshi Higuchi, Shinsuke Takada, Shiro Hanai
[*1]Wood Research Institute, Kyoto University, [*2]Faculty of Agriculture, Kinki University, [*3]Takara Shuzo Co. Ltd.
Keywords: *Betula Tauschii*, *Larix Kaempferi*, SEM, TEM, pulping

1982-204
Fusarium 属菌の生産するリグニン関連芳香族化合物の分解に関与する酵素系について
岩原章二郎
香川大学農学部
On the enzymes produced by *Fusarium* species that participate in degradation of lignin-related aromatic compounds
Shojiro Iwahara
Faculty of Agriculture, Kagawa University
Keywords: laccase, pinoresinol, syringaresinol, UV absorption spectroscopy

1982-205
Phanerochaete chrysosporium のピリジン補酵素代謝　—リグニン分解との関連性について
桑原正章、麻田恭彦、石田　豊、河上智栄美、赤池嘉彦
香川大学農学部

Metabolism of pyridine coenzymes in *Phanerochaete chrysosporium*, –In relation to lignin degradation
Masaaki Kuwahara, Yasuhiko Asada, Yutaka Ishida, Chiemi Kawakami, Yoshihiko Akaike
Faculty of Agriculture, Kagawa University
Keywords: *Aspergillus* sp., radiotracer, NAD, NADP

1982-206
Guaiacylglycerol−β-guaiacyl ether の分解に関与する酵素系について
沖　妙、新本美智枝、石川久雄
愛媛大学農学部
Enzymes involved in the degradation of guaiacylglycerol-β-guaiacyl ether
Tae Oki, Michie Shinmoto, Hisao Ishikawa
Faculty of Agriculture, Ehime University
Keywords: *Pinus densiflora, Phanerochaete chrysosporium, Lentinus edodes,* peroxidase, laccase

1982-207
木材腐朽菌によるリグニンモデル化合物の代謝について
榎　章郎[*1]、田中裕美[*1]、高橋旨象[*2]、布施五郎[*1]
[*1] 近畿大学農学部、[*1] 京都大学木材研究所
Metabolism of lignin model compounds by wood rotting fungi
Akio Enoki[*1], Hiromi Tanaka[*1], Munezoh Takahashi[*2], Goro Fuse[*1]
[*1]Faculty of Agriculture, Kinki University, [*2]Wood Research Institute, Kyoto University
Keywords: white rot fungi, brown rot fungi

1982-208
Phanerochaete chrysosporium による 5-carboxyprotocatechuic acid の分解
梅澤俊明、樋口隆昌
京都大学木材研究所
Degradation of 5-carboxyprotocatechuic acid by *Phanerochaete chrysosporium*
Toshiaki Umezawa, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: 5,5’-dehydrodivanillic acid, phenylcoumaran

1982-209
Phanerochaete chrysosporium によるシリンガレジノールの分解
釜谷保志、樋口隆昌
京都大学木材研究所
Degradation of syringaresinol by *Phanerochaete chrysosporium*
Yasushi Kamaya, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: ^{1}H-NMR, ^{13}C-NMR,

1982-210
リグニンとリグニンモデル化合物の光増感剤及びヒドロキシルラジカルによる分解
久津木英俊[*1*2]、M. H. Gold[*2]
[*1] 京都大学木材研究所、[*2] オレゴン大学院センター
Degradation of lignin and lignin model compounds by photosensitizer and hydroxyl radical
Hidetoshi Kutsuki[*1*2], Michael H. Gold[*2]
[*1*2]Wood Research Institute, Kyoto University, [*2]Oregon Graduate Center
Keywords: *Phanerochaete chrysosporium*, nonphenolic lignin model compounds, singlet oxygen, ^{14}C-DHP

1982-211
カワラタケ生育時に分泌される酵素類について
諸星紀幸、中村　剛、村磯知採、原口隆英
東京農工大学農学部

Characterization of enzymes secreted during the growth of *Coriolus versicolor*
Noriyuki Morohoshi, Tuyoshi Nakamura, Chidori Muraiso, Takafusa Haraguchi
Faculty of Agriculture, Tokyo University of Agriculture and Technology
Keywords: tyrosinase, laccase, cellulase, pectinase, protease, gel filtration

1982-212
カワラタケラッカーゼによるリグニンの変化（第 3 報）—精製ラッカ−ゼのリグニンに対する反応性—
割石博之、藤田佳代、諸星紀幸、原口隆英
東京農工大学農学部
Changes of lignin by the treatment with laccase from *Coriolus versicolor* (III), Reactivity of purified laccase with lignin
Hiroyuki Wariishi, Kayo Fujita, Noriyuki Morohoshi, Takafusa Haraguchi
Faculty of Agriculture, Tokyo University of Agriculture and Technology
Keywords: Yezo spruce, *Picea jezoensis*, BNL, MWL, LCC, ESR

1982-213
白腐れ菌菌体内の酸素添加酵素について
田部眞哉、野中久美雄、原口隆英
東京農工大学農学部
Characterization of intracellular oxygenation enzyme of white rot fungi
Shinya Tabe, Kumio Nonaka, Takafusa Haraguchi
Faculty of Agriculture, Tokyo University of Agriculture and Technology
Keywords: *Pycnoporus coccineus*, *Stereum frustulosum*, catechol, protocatechuic acid, vanillic acid

1982-214
Lentinus edodes の広葉樹材への作用とそのクラフトパルプ化
赤松　勲、上嶋　洋、藤井利郎、小林　武
四国工業技術試験所
Treatment of hardwood with *Lentinus edodes* and its kraft pulping
Isao Akamatsu, Hiroshi Kamishima, Toshiro Fujii, Takeshi Kobayashi
Government Industrial Research Institute, Shikoku
Keywords: *Quercus acutissima*, *Quercus serrata*, X-ray diffraction, cellulose crystalinity, MWL

1982-215
Erwinia carotovora を用いた発酵精練によるコウゾのパルプ化
小林良生、松尾隆吉
四国工業技術試験所
Pulping of Kozo bast by retting with *Ervinia carotovora*
Yoshio Kobayashi, Ryukichi Matsuo
Government Industrial Research Institute, Shikoku
Keywords: *Broussonetia kazinoki* × *B. papyrifera*, retting, *Erwinia carotovora*, brightness

1982-216
パルプ廃液の新しい微生物処理法へのアプローチ
鮫島一彦、高村憲男
高知大学農学部
Approach to the new microbiological treatment of pulping effluent
Kazuhiko Sameshima, Norio Takamura
Faculty of Agriculture, Kochi University
Keywords: BOD, wood rotting fungi,

1982-217
特別講演、バイオマス特にリグニン経由化学製品開発の世界的動向
鈴木　明

野口研究所

Invited lecture: World trend of research and development of chemicals from biomass and especially from lignin

Akira Suzuki
Noguchi Institute

Keywords: hydrocracking, ethanol production,

第 28 回（1983.10.7-8）北海道大学農学部

1983-101
オートラジオグラフイーからみた細胞間層と二次壁の木化
高部圭司、藤田　稔、佐伯　浩、原田　浩
京都大学農学部
Lignification of middle lamella and secondary wall investigated by autoradiography
Keiji Takabe, Minoru Fujita, Hiroshi Saiki, Hiroshi Harada
Faculty of Agriculture, Kyoto University
Keywords: *Cryptomeria japonica,* UV microscopy, fluorescent microscopy, ^{3}H-phenylalanine
1983-102
細胞壁形成、とくに木化の細胞学的検討
藤田　稔、高部圭司、佐伯　浩、原田　浩
京都大学農学部
Cytological studies on cell wall formation especially on lignification
Minoru Fujita, Keiji Takabe, Hiroshi Saiki, Hiroshi Harada
Faculty of Agriculture, Kyoto University
Keywords: *Populus euramericana*, *Cryptomeria japonica,* reaction wood, microautoradiography,

1983-103
オートラジオグラフイーからみたマツ属放射柔細胞壁の木化
山本幸一^{*1}、深沢和三^{*2}、石田茂雄^{*2}
^{*1} 林業試験場、^{*2} 北海道大学農学部
Studies on lignification of ray parenchyma wall of pine by microautoradiography
Koichi Yamamoto^{*1}, Kazumi Fukazawa^{*2}, Shigeo Ishida^{*2}
^{*1}Forestry and Forest Products Research Institute, ^{*2}Faculty of Agriculture Hokkaido University
Keywords: *Pinus strobes, Pinus densiflora, Pinus banksiana,* ^{3}H-phenylalanine, ^{14}C-glucose

1983-104
カラマツ 2 次師部の厚壁細胞の木化経過
今川一志、深沢和三、石田茂雄
北海道大学農学部
Lignification process of sclerenchyma cell of larch secondary phloem
Kazushi Imagawa, Kazumi Fukazawa, Shigeo Ishida
Faculty of Agriculture, Hokkaido University
Keywords: *Larix leptolepis,* screleid fiber, UV microscope

1983-105
紫外及び電子顕微鏡による細胞壁中のリグニン分布の観察
広居忠量、藤井智之
林業試験場
Observation of lignin distribution across cell wall by UV microscopy and electron microscopy
Tadakazu Hiroi, Tomoyuki Fujii
Forestry and Forest Products Research Institute
Keywords: *Fagus crenata*, guaiacyl lignin, syringyl lignin, electron microphotography, UV microphotography

1983-106
広葉樹材複合細胞間層リグニンの性状について
飯塚堯介、中野準三
東京大学農学部
Characterization of lignin in compound middle lamella of hardwood
Gyosuke Meshitsuka, Junzo Nakano
Faculty of Agriculture, the University of Tokyo

Keywords: *Betula maximowiczii*, nitrobenzene oxidation, Klason lignin, condensed structure

1983-107
ソルボリシスリグニン　—低分子量フラクションについて—
佐野嘉拓、遠藤博之、榊原　彰
北海道大学農学部
Solvolysis lignin. -Characterization of low molecular weight fraction
Yoshihiro Sano, Hiroyuki Endo, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: *Quercus crispula, p*-cresol, ^{1}H-NMR, ^{13}C-NMR,

1983-108
硫酸リグニンの化学構造
安田征市、寺島典二、浜中　篤
名古屋大学農学部
Chemical structures of sulfuric acid lignin
Seiichi Yasuda, Noritsugu Terashima, Atsushi Hamanaka.
Faculty of Agriculture, Nagoya University
Keywords: *Pinus densiflora*, carbohydrates, arylglycerol-β-aryl ether, ^{1}H-NMR, nitrobenzene oxidation, permanganate oxidation, condensation reaction

1983-109
トリメチルクロルシラン／ヨウ化ナトリウムによるリグニン中のエーテル結合の選択的開裂
近藤哲男、飯塚堯介、中野準三
東京大学農学部
Selective cleavage of ether linkage in lignin by trimethylchlorosilane/sodium iodide
Tetsuo Kondo, Gyosuke Meshitsuka, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: *Picea jezoensis,* MWL, guaiacylglycerol-β–guaiacyl ether, gel filtration chromatography

1983-110
アルカリ蒸解時のリグニンの縮合反応について　—特にコニフェリルアルコールの蒸解時の役割—
近藤隆一郎[*1]、J.F. McCarthy[*2]
[*1] 九州大学農学部、[*2] ワシントン大学
Condensation reactions of lignin during alkaline pulping. -Role of coniferyl alcohol during cooking
Ryuichiro Kondo[*1], J. F. McCarthy[*2]
[*1]Faculty of Agriculture, Kyushu University, [*2]University of Washington
Keywords: western hemlock, *Thuja heterophylla,* soda cooking, soda AQ cooking, kraft cooking, gel filtration chromatography

1983-111
リグニンの酸化分解（VI）　—ヒドロキシラジカルとリグニンの芳香核との反応—
辰巳憲司[*1]、寺島典二[*2]
[*1] 公害資源研究所, [*2] 名古屋大学農学部
Oxidative degradation of lignin (VI), —Reaction of aromatic ring in lignin with a hydroxyl radical
Kenji Tatsumi[*1], Noritsugu Terashima[*2]
[*1]National Research Institute for Pollution and Resources, [*2]Faculty of Agriculture, Nagoya University
Keywords: veratric acid, UV irradiation, gas chromatography, mass spectrometry

1983-112
分子軌道法によるリグニンの反応性の検討
飯山賢治
東京大学農学部
Studies on reactivity of lignin by molecular orbital method

Kenji Iiyama
Faculty of Agriculture, the University of Tokyo
Keywords: biphenyl, apocynol, cooking with nucleophilic additives

1983-113
リグニン吸着水の ^{1}H 核磁気緩和
畠山兵衛[*1]、岩田ひろ[*1]、畠山立子[*2]
[*1] 製品科学研究所、[*2] 繊維高分子材料研究所
Proton nuclear magnetic relaxation of adsorbed water in lignin
Hyoe Hatakeyama[*1], Hiro Iwata[*1], Tatsuko Hatakeyama[*2]
[*1]Industrial Products Research Institute, [*2]Research Institute for Polymers and Textiles
Keywords: *Hyderia decuurens* , dioxane lignin, DSC

1983-114
リグノスルホン酸塩の吸湿と粘弾性
矢野彰一郎[*1]、Mikael Rigdahl[*2], Petter Kolseth[*2], Alf de Ruvo[*2]
[*1] 製品科学研究所、[*2]STFI (Sweden)
Moisture adsorption and viscoelasticity of lignosulfonate
Shoichiro Yano[*1], Mikael Rigdahl[*2], Petter Kolseth[*2], Alf de Ruvo[*2]
[*1]Industrial Products Research Institute, [*2]STFI (Sweden)
Keywords: *Picea abies*, adsorption isotherm

1983-115
特別講演、Biomass の加水分解工程
小林達吉
東京教育大学名誉教授
Invited lecture ; Hydrolysis process of biomass
Tatsukichi Kobayashi
Professor emeritus, Tokyo University of Education

1983-201
カワラタケ菌体外分泌蛋白の 2 次元電気泳動
諸星紀幸、割石博之、原口隆英
東京農工大学農学部
Two dimensional electrophoresis of the proteins secreted by *Coriolus versicolor*
Noriyuki Morohoshi, Hiroyuki Wariishi, Takafusa Haraguchi
Faculty of Agriculture, Tokyo University of Agricultue and Technology
Keywords: laccase, cellulase, β–glucosidase, xylanase, affinity chromatography

1983-202
Guaiacylglycerol-β-guaiacyl ether の生分解に関与する酵素系について
沖 妙、新本美智枝、石川久雄
愛媛大学農学部
Studies on the enzymes involved in the biodegradation of guaiacylglycerol-β–guaiacyl ether
Tae Oki, Michie Shinmoto, Hisao Ishikawa
Faculty of Agriculture, Ehime University
Keywords: *Coprinus aff ellisii, Phanerochaete chrysosporium*, *Coriolus versicolor,*
Irpex lacteus, Schizophyllum commune

1983-203
Phanerochaete chrysosporium による β–*O*–4 及び β–1 型二量体の分解における $^{18}\mathrm{O}_2$ の取り込み
梅澤俊明[*1]、樋口隆昌[*1]、中坪文明[*2]
[*1] 京都大学木材研究所、[*2] 京都大学農学部
Incorporation of $^{18}\mathrm{O}_2$ during the degradation of β-O-4 and β-1 type dimers by *Phanerochaete chrysosporium*

Toshiaki Umezawa*1, Takayoshi Higuchi*1, Fumiaki Nakatsubo*2
*1Wood Research Institute, Kyoto University, *2Faculty of Agriculture, Kyoto University
Keywords: ^{1}H-NMR, mass spectrometry

1983-204
カンバ材リグニンの生分解
寺沢　実*1、D. Tai*2、C. L. Chen*3、H-m. Chang*3、T. K. KirK*4
*1 帯広畜産大学、*2 南京林産工業学院、*3 ノースカロライナ州立大学、*4USDA 林産物研究所
Biodegradation of birch lignin
Minoru Terasawa*1, D. Tai*2, C.L. Chen*3, H-m. Chang*3, T. K. Kirk*4
*1Obihiro University of Agriculture and Veterinary Medicine, *2Nanjin University of Forest Industry, *3North Carolina State University, *4Forest Products Laboratory Madison
Keywords: *Betula platyphylla, Phanerochaete chrysosporium*, degradation products

1983-205
木材の酵素による加水分解　—無機塩存在下での蒸煮・爆砕処理の効果—
須藤賢一、石井　忠、志水一允、藤井智之、長沢定男
林業試験場
Enzymatic hydrolysis of wood. -Effects of steam-explosion under the presence of inorganic salts
Kenichi Sudo, Tadashi Ishii, Kazumasa Shimizu, Tomoyuki Fujii, Sadao Nagasawa
Forestry and Forest Products Research Institute
Keywords: *Betula platyphylla, Fagus crenata*, *Aesculus turbinate*, *Larix Kaempferi,* aluminium chloride, ammonium chloride,

1983-206
リグニン—糖間の物理および化学的結合について
Lam Thi Bach Tuyet、飯山賢治、中野準三
東京大学農学部
Studies on the physical and chemical associations between lignin and carbohydrate
Lam Thi Bach Tuyet, Kenji Iiyama, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: refiner mechanical pulp, carboxymethylation, gel filtration, ^{1}H-NMR,

1983-207
ヘミセルロース・リグニン結合体に関する研究（その 10）—バガス Björkman LCC の性質—
加藤　厚、東　順一、越島哲夫
京都大学木材研究所
Studies on hemicellulose-lignin bond (X), Characterization of bagasse Björkman LCC
Atsushi Kato, Junichi Azuma, Tetsuo Koshijima
Wood Research Institute, Kyoto University
Keywords: *Saccharum* sp., ferulic acid, coumaric acid, gel filtration, ^{13}C-NMR

1983-208
Klason Lignin に残存する炭水化物について
松本雄二、寺澤一雄、石津　敦、中野準三
東京大学農学部
Studies on the carbohydrate remaining in Klason lignin
Yuji Matsumoto, Kazuo Terasawa, Atsushi Ishizu, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: *Picea jezoensis*, *Betula* sp., ozone degradation,

1983-209
白色腐朽菌のポプラチップへの作用と同菌による部分分解材の TMP 化
赤松　勲、吉原一年、上嶋　洋、藤井利郎

四国工業技術試験所
Treatment of poplar chips with white rot fungi and production of TMP from the treated chips
Isao Akamatsu, Kazutoshi Yoshihara, Hiroshi Kamishima, Toshiro Fujii
Government Industrial Research Institute, Shikoku
Keywords: *Populus* sp., defibration energy, pulp properties

1983-210
前加水分解処理（アスプルンド法）残渣パルプの性質
島田謹爾、高野　勲、宇佐見国典、長沢定男、須藤賢一、志水一允
林業試験場
Characterization of prehydrolysis (Asplund) pulp
Kinji Shimada, Isao Takano, Kuninori Usami, Sadao Nagasawa, Kenichi Sudo, Kazumasa Shimizu
Forestry and Forest Products Research Institute
Keywords: *Betula Tauschii*, *Pinus densiflora, Fagus crenata, Larix Kaempferi,* chlorine, chlorine dioxide, sodium hypochlorite, strength properties

1983-211
過酸化水素—アルカリ法（PA 法）による沖縄産ギンネムのパルプ化
金沢健治[*1]、御田昭雄[*1]、柏原　進[*1]、原　信治[*2]、浅見明彦[*2]
[*1] 化学技術研究所、[*2] 東海パルプ株式会社
Peroxide-alkali pulping (PA process) of lead tree (*Leucaena leucocephala*)
Kenji Kanazawa[*1], Akio Mita[*1], Susumu Kashiwabara[*1], Shinji Hara[*2], Akihiko Asami[*2]
[*1]National Chemical Laboratory for Industry, [*2]Tokai pulp Co. Ltd.
Keywords: bleachability, EDTA, anthraquinone

1983-212
アルカリ酸素蒸解に関する研究（第 7 報）—稲わらパルプの酸化漂白—
戸坂圀夫、林　治助
北海道大学工学部
Studies on alkali-oxygen pulping (VII), -Oxidative bleaching of rice straw pulp—
Kunio Tosaka, Jisuke Hayashi
Faculty of Engineering, Hokkaido University
Keywords: *Oryza sativa*, ozone bleaching, alkaline hydrogen peroxide bleaching, brightness

1983-213
ネマガリタケのソルボリシスパルプ化
中村敏也、榊原　彰
北海道大学農学部
Solvolysis pulping of *Sasa kurilensis*
Toshiya Nakamura, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: cresol, brightness, biomass refinery

1983-214
高歩留 SP 廃液を利用した耐水性接着剤の製造
境　一男、佐藤　裕、成田　升、下田　優
王子建材工業株式会社
Preparation of waterproof adhesives from high yield sulfite pulp effluent
Kazuo Sakai, Hiroshi Sato, Masu Narita, Suguru Shimoda
Oji Kenzai Co. Ltd.
Keywords: phenol, lauan plywood, birch plywood, larch plywood, particleboard,

1983-215
カラマツ樹皮の水酸化ナトリウム抽出物を利用した接着剤の製造

窪田　実、平田三郎、斉藤　勝、駒沢克己、青山政和
北海道立林産試験場
Preparation of adhesives from sodium hydroxide extracts of larch bark
Minoru Kubota, Saburo Hirata, Masaru Saito, Katsumi Komazawa, Masakazu Aoyama
Hokkaido Forest Products Research Institute
Keywords: *Larix Kaempferi,* polyphenol,

1983-216
紙・パルプ廃液からの活性炭の製造
里中聖一、磯部泰佐、香山　彊
北海道大学農学部
Production of activated carbon from pulp and paper mill effluent
Seiichi Satonaka, Taisuke Isobe, Tsutomu Kayama
Faculty of Agriculture, Hokkaido University
Keywords: *Picea Glehnii, Betula Tauschii*, *Quercus crispula,*

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1984-101
広葉樹複合細胞間層リグニンの性状について（第 2 報）
飯塚堯介、中野準三
東京大学農学部
Characterization of lignin in compound middle lamella of hardwood (II)
Gyosuke Meshitsuka, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: *Betula maximowicziana*, *BetulaTauschii*, fiber, soft xylem, permanganate oxidation, nitrobenzene oxidation

1984-102
針葉樹プロトリグニンの芳香核縮合度について
船岡正光、阿部　勲
三重大学農学部
Degree of condensation of aromatic rings in softwood protolignin
Masamitsu Funaoka, Isao Abe
Faculty of Agriculture, Mie University
Keywords: *Chamaecyparis obtuse,* nuclear exchange method, condensation degree

1984-103
スギ穿孔性害虫被害材リグニンの化学的特性
島田謹爾、西田篤実、高野　勲、宇佐美国典
林業試験場
Chemical characteristics of lignin in the wood damaged by boring insect
Kinji Shimada, Atsumi Nishida, Isao Takano, Kuninori Usami
Forestry and Forest Products Research Institute
Keywords: *Anaglyptus subfasciatus, Resseliella odai, Epi-notia granitalis*, permanganate oxidation

1984-104
硫酸リグニンの化学構造　— 1,2−ジアリール-1,3−プロパンジオールと硫酸との反応
安田征市，足立久美子、寺島典二、太田勝人
名古屋大学農学部
Chemical structures of sulfuric acid lignin. —Reactions of 1,2-diaryl- 1,3-propanediol with sulfuric acid
Seiichi Yasuda, Kumiko Adachi, Noritsugu Terashima, Katsuhito Oota
Faculty of Agriculture, Nagoya University
Keywords: pinoresinol,

1984-105
リグニン・ヘミセルロース結合体の簡便な調製法とその構造
東　順一[*1]、渡辺隆司[*1*2]、越島哲夫[*1]
[*1] 京都大学木材研究所、[*2] 山陽国策パルプ株式会社
Simple preparation of lignin hemicellulose complex and its chemical structure
Junichi Azuma[*1], Takashi Watanabe[*1*2], Tetsuo Koshijima[*1]
[*1]Wood Research Institute, Kyoto University, [*2]Sanyo Kokusaku Pulp Co. Ltd.
Keywords: *Pinus densiflora,* Björkman LCC, ion exchange chromatography, ^{13}C-NMR

1984-106
クラフトパルプにおけるリグニンと炭水化物の結合
磯貝　明、石津　敦、中野準三
東京大学農学部
Linkages between lignin and carbohydrate in kraft pulp
Akira Isogai, Atsushi Ishizu, Junzo Nakano

Faculty of Agriculture, the University of Tokyo
Keywords: gel permeation chromatography, lignin cellulose linkage, lignin hemicellulose linkage

1984-107
リグニンの酸化分解（VII）ヒドロキシラジカルによるリグニンの分解
辰巳憲司[*1]、寺島典二[*2]
[*1] 公害資源研究所, [*2] 名古屋大学農学部
Oxidative degradation of lignin. VII. Degradation of lignin with a hydroxyl radical
Kenji Tatsumi[*1], Noritsugu Terashima[*2]
[*1]National Research Institute for Pollution and Resources, [*2]Faculty of Agriculture, Nagoya University
Keywords: aromatic ring, UV irradiation, lignin model compounds, mass spectrometry

1984-108
好アルカリ性細菌によるリグニンモデル化合物の分解
川上日出国、近藤規子
名古屋大学農学部
Degradation of lignin model compounds by alkalophilic bacteria
Hidekuni Kawakami, Noriko Kondo
Faculty of Agriculture, Nagoya University
Keywords: *β-O*-4 dimer, biphenyl compounds, mass spectrometry, *Pseudomonas ovalis*

1984-109
菌体外酵素による Guaiacylglycerol-β-guaiacyl ether の生分解
沖　妙、新本美智枝、石川久雄
愛媛大学農学部
Biodegradation of guaiacylglycerol-β-guaiacyl ether by extracellular enzyme
Tae Oki, Michie Shinmoto, Hisao Ishikawa
Faculty of Agriculture, Ehime University
Keywords: *Coriolus versicolor, Irpex lacteus, Phanerochaete chrysosporium, Coprinus off ellisii*, dioxane lignin

1984-110
カワラタケ菌体外酵素によるリグニンモデル化合物の分解
諸星紀幸、原口隆英
東京農工大学農学部
Degradation of lignin model compounds by the extracellular enzyme of *Coriolus versicolor*
Noriyuki Morohoshi, Takafusa Haraguchi
Faculty of Agriculture, Tokyo University of Agriculture and Technology
Keywords: *Coriolus versicolor,* laccase Ⅲ, syringylglycerol-β-(2,6-dimethoxyphenyl) ether

1984-111
α-*O*-4 型及び α 位にケトンを有する β-*O*-4 型リグノールの *Fusarium solani* M-13-1 による分解
片山健至[*1]、山田康博[*1]、十河村男[*1]、樋口隆昌[*2]
[*1] 香川大学農学部、[*2] 京都大学木材研究所
Degradation of an α-*O*-4 type lignol and β-*O*-4 type lignol with α-ketone by *Fusarium solani* M-13-1.
Takeshi Katayama[*1], Yasuhiro Yamada[*1], Murao Sogo[*1], Takayoshi Higuchi[*2]
[*1]Faculty of Agriculture, Kagawa University, [*2]Wood Research Institute, Kyoto University
Keywords: dilignols, non-cyclic benzyl ether, trilignols, mass spectrometry, ^{13}C-NMR,

1984-112
4-エトキシ-3-メトキシフエニルグリセロール-β-シリンガアルデヒドエーテルのカワラタケによる分解
河合真吾、梅沢俊明、樋口隆昌
京都大学木材研究所
Degradation of 4-ethoxy-3-methoxyphenylglycerol-β-syringaldehyde ether by *Coriolus versicolor*

Shingo Kawai, Toshiaki Umezawa, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: biodegradation, lignin substructure model compound, *Phanerochaete chrysosporium, Pseudomonas putida*, TLC, NMR, GC-MS,

1984-113
Phanerochaete chrysosporium による β–□-4 結合の開裂とアリールグリセロールの生成機構について
梅澤俊明、樋口隆昌
京都大学木材研究所
Cleavage of β–□-4 bond and formation of arylglycerol by *Phanerochaete chrysosporium*
Toshiaki Umezawa, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: ^{18}O tracer, TLC, GC-MS

1984-114
リグニン分解へのバイオミメティックアプローチ(I) —リグニンモデル化合物の分解反応に及ぼすヘミンの触媒効果
島田幹夫[*1]、波部　豪[*1]、樋口隆昌[*1]、岡本　忠[*2]
[*1] 京都大学木材研究所、[*2] 京大化学研究所
Biomimetic approach to the degradation of lignin (I), Catalytic effect of hemin on the degradation of lignin model compounds
Mikio Shimada[*1], Tsuyoshi Habe[*1], Takayoshi Higuchi[*1], Tadashi Okamoto[*2]
[*1]Wood Research Institute, Kyoto University, [*2]Institute for Chemical Research, Kyoto University
Keywords: iron porphyrin, cytochrome, peroxidase, catalase

1984-115
リグニン分解へのバイオミメティックアプローチ（II） —リグニン分解酵素及び酵素モデル触媒による重水素化リグニンモデル化合物の分解
波部　豪、島田幹夫、樋口隆昌
京都大学木材研究所
Biomimetic approach to the degradation of lignin (II), -Degradation of deuterated lignin model compounds by lignin degrading enzyme and enzyme model catalyst
Tsuyoshi Habe, Mikio Shimada, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: *Phanerochaete chrysosporium*, hemin

1984-116
特別講演、リグニン化学構造研究の回顧
榊原　彰
北海道大学農学部
Invited lecture; Retrospection on the research of lignin chemical structure
Akira Sakakibara
Faculty of Agriculture, Hokkaido University

1984-201
爆砕処理による木質系物質の利用
志水一允[*1]、須藤賢一[*1]、長沢定男[*1]、島田規男[*2]、菅原一晃[*3]
[*1] 林業試験場、[*2] 東和化成、[*3] 三菱重工
Utilization of woody biomass by steam explosion
Kazumasa Shimizu[*1], Kenichi Sudo[*1], Sadao Nagasawa[*1], *Norio Shimada[*2], Kazuaki Sugawara[*3]
[*1]Forestry and Forest Products Research Institute, [*2]Towa-Kasei Co. Ltd., [*3]Mitsubishi Heavy Industries Co. Ltd.
Keywords: *Betula Tauschii*, *Fagus crenata, Quercus serrata, Castanopsis cuspidate,* GPC

1984-202
A Solid state CP/MAS NMR-study of a product synthesized from lignin and sulphur
K. Levon, B. Hortling, J.J. Lindberg
ヘルシンキ大学 University of Helsinki
Keywords: sulphur lignin, poly(phenylene)sulphides, lignosulphonate, solution NMR

1984-203
リグニン関連型構造を有するコレステリルエステルの合成とその液晶性
春日和行、畠山兵衛
製品科学研究所
Synthesis of cholesteryl ester with lignin-related structure and its characteristics as liquid crystal
Kazuyuki Kasuga, Hyoe Hatakeyama
Industrial Products Research Institute
Keywords: 4-*n*-alkoxybenzoic acid derivative, polarization microscope, DSC

1984-204
水-リグノスルホン酸 Na 塩混合系の DSC 及び ^{23}Na−NMR
畠山兵衛[*1]、広瀬重雄[*1]、中村邦雄[*2]、畠山立子[*3]
製品科学研究所、神奈川県工業試験所、繊維高分子材料研究所
DSC and ^{23}Na−NMR studies of the water-sodium lignosulphonate system
Hyoe Hatakeyama[*1], Shigeo Hirose[*1], Kunio Nakamura[*2], Tatsuko Hatakeyama[*3]
[*1]Industrial Products Research Institute, [*2]Kanagawa Industrial Technology Center, [*3]Institute for Textiles and Polymers
Keywords: non-freezing water, freezing bound water,

1984-205
マニラ麻の Bio−RMP 化について
赤松　勲、上島　洋、藤井利郎、吉原一年
四国工業技術試験所
Preparation of bio-refiner mechanical pulp from Manila hemp
Susumu Akamatsu, Hiroshi Kamishima, Toshiro Fujii, Kazutoshi Yoshihara
Government Industrial Research Institute, Shikoku
Keywords: Bio-RMP, Manila hemp, white rot fungi, *Coriolus hirstus*

1984-206
ソルボリシスパルプの組織化学的研究
枝重有祐、榊原　彰
北海道大学農学部
Histochemical study of solvolysis pulp
Yusuke Edashige, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: beech, *Fagus crenata,* sapwood, heartwood, UV microscopy

1984-207
加溶媒分解におけるヘミセルロースの挙動
小沢修二、武山浩武、榊原　彰
北海道大学農学部
Behaviors of hemicellulose during solvolysis
Shuji Ozawa, Hirotake Takeyama, Akira Sakakibara
Faculty of Agriculture, Hokkaido University
Keywords: *Betula Tauschii*, cresol, GPC, ^{1}H-NMR, ^{13}C-NMR, MS

1984-208
有機溶媒と亜硫酸塩による脱リグニン（III）イソプロピルアルコール—亜硫酸塩セミケミカルパルプ化におけ

る樹種特性
文 星筆、近藤隆一郎、坂井克己、今村博之
九州大学農学部
Delignification with organic solvents and bisulfite (III), Characteristics of wood species on semichemical pulping with isopropyl alcohol and bisulfite
Sung-Phil Mung, Ryuichiro Kondo, Kokki Sakai, Hiroyuki Imamura
Faculty of Agriculture, Kyushu University
Keywords: softwood, hardwood, tropical wood,

1984-209
アルカリ蒸解における針葉樹型および広葉樹型リグニンの反応性の差異
近藤隆一郎、堤 祐司、野口浩司、今村博之
九州大学農学部
Differences in reactivity between softwood and hardwood lignins during alkaline pulping
Ryuichiro Kondo, Yuji Tsutsumi, Koji Noguchi, Hiroyuki Imamura
Faculty of Agriculture, Kyushu University
Keywords: kinetics, guaiacylglycerol-β–guaiacyl ether, syringylglycerol-β–syringyl ether, β–aryl ether cleavage,

1984-210
Modified Kraft Pulplng. A way to decrease lignin content and improve pulp quality
Peter Sandström
STFI, Swedish Pulp and Paper Research Institute
Keywords: initial phase, bulk delignification, final phase, effective alkali

1984-211
酸素・アルカリ蒸解の蒸解要因（10）コバルト・アミノアルコール錯体の脱リグニン促進効果
目黒貞利、今村博之
九州大学農学部
Factors influencing oxygen-alkali cooking (X), Delignification enhancement by the addition of cobalt-amino alcohol complex
Sadatoshi Meguro, Hiroyuki Imamura
Faculty of Agriculture, Kyushu University
Keywords: *Betula Tauschii*, Co-salen, Co-triethanolamine complex,

1984-212
GP リグニンのニトロベンゼン酸化について
平島英則[*1]、住本昌之[*2]
[*1] 片山化学工業株式会社、[*2] 九州大学農学部
Nitrobenzene oxidation of GP lignin
Hidenori Hirashima[*1], *Masashi Sumimoto[*2]
[*1]Katayama Chemical Industries Co. Ltd, [*2]Faculty of Agriculture, Kyushu University
Keywords: *Pinus densiflora*, bleaching, brightness

1984-213
脱リグニン反応に及ぼす超音波照射の影響（第 2 報）超音波照射下におけるリグニンの挙動
譚 国民、安田征市、寺島典二
名古屋大学農学部
Effect of ultrasonic irradiation on delignification reaction (II), Behavior of lignin during delignification under ultrasonic irradiation
Guo-Min Tan, Seiichi Yasuda, Noritsugu Terashima
Faculty of Agriculture, Nagoya University
Keywords: *Pinus densiflora*, MWL, guaiacylglycerol-β–guaiacyl ether, calcium hypochlorite

1984-214

バガスの UPAP の漂白の無塩素化について

御田昭雄、柏原 進

化学技術研究所

Nonchlorine bleaching of UPAP from bagasse

Akio Mita, Susumu Kashiwabara

National Chemical Laboratory for Industry

Keywords: AQ, AP, brightness

1984-215

晒排液中の突然変異原性に関する研究（第 1 報）各種の親核試薬による突然変異原性の解毒機構

橘 燦郎[*1]、J. Santodonato[*2]、C. W. Dence[*3]

[*1] 九州大学農学部、[*2] シラキユース大学、[*3] ニューヨーク州立大学

Studies on the mutagenicity of bleach effluent (I), Mechanism of the detoxication of mutagenicity by nucleophilic reagents

Sanro Tachibana[*1], J. Santodonato[*2], C. W. Dence[*3]

[*1]Faculty of Agriculture, Kyushu University, [*2]University of Syracuse, [*3]State University of New York

Keywords: *Pinus virginiana*, *Pinus taeda,* 2-chloropropenal, chloroacetone, chloro-*o*-benzoquinone,

1984-216

招待講演、

Soda-AQ／oxygen pulping process as an alternative to kraft process for production of bleached pulp from softwood

Y. C. Tsai, N. H. Shin, H.–m. Chang, J. S. Gratzl

ノースカロライナ州立大学

Invited lecture;

Y. C. Tsai, N. H. Shin, H.-m. Chang, J. S. Gratzl

North Carolina State University

Keywords: viscosity, brightness,

第30回（1985.11.6-7）高知会館

1985-101
スギ細胞壁の木化とペルオキシダーゼ活性の分布
高部圭司、原田　浩
京都大学農学部
Lignification and distribution of peroxidase activity in Japanese cedar cell wall
Keiji Takabe, Hiroshi Harada
Faculty of Agriculture, Kyoto University
Keywords: *Cryptomeria japonica,* osmium black, electron micrograph, lignin skeleton,

1985-102
カラマツ師部の厚壁細胞の木化（予報）
今川一志、深沢和三
北海道大学農学部
Lignification of fiber sclereid in the phloem of larch (Preliminary report)
Kazushi Imagawa, Kazumi Fukazawa
Faculty of Agriculture, Hokkaido University
Keywords: *Larix leptolepis*, UV micrograph, lignin distribution, differentiation

1985-103
広葉樹リグニン中のグアヤシルおよびシリンギル構造の選択的標識
寺島典二[*1]、福島和彦[*1]、高部圭司[*2]
名古屋大学農学部、京都大学農学部
Selective radio-labeling of guaiacyl and syringyl structures in hardwood lignin
Noritsugu Terashima[*1], Kazuhiko Fukushima[*1], Keiji Takabe[*2]
[*1]Faculty of Agriculture, Nagoya University, [*2]Faculty of Agriculture, Kyoto University
Keywords: magnolia, *Magnolia kobus*, oxford poplar, *Populus Maximowiczii* X *Populus belorinensis,* autoradiography, guaiacyl unit, syringyl unit, ^{3}H-coniferin, ^{3}H-syringin

1985-104
リグニンモデル化合物の合成とそのニトロベンゼン酸化について
季　典艶、橘　燦郎、住本昌之
九州大学農学部
Synthesis of lignin model compounds and their nitrobenzene oxidation
Dian Yan Lee, Sanro Tachibana, Masashi Sumimoto
Faculty of Agriculture, Kyushu University
Keywords: guaiacylglycerol-β-coniferyl ether, guaiacylglycerol-β-guaiacyl ether, nitrobenzene oxidation, ^{1}H-NMR, mass spectrometry

1985-105
硫酸リグニンの化学構造　―硫酸溶液中におけるシリンギルアルコールの反応とグアヤシルおよびシリンギル核の反応性
安田征市、太田勝人
名古屋大学農学部
Chemical structures of sulfuric acid lignin. ―Reactions of syringyl alcohol and reactivity of guaiacyl and syringyl nucleus in sulfuric acid
Seiichi Yasuda, Katsuhito Oota
Faculty of Agriculture, Nagoya University
Keywords: condensation, hardwood lignin, guaiacyl nucleus, syringyl nucleus, ^{13}C-NMR

1985-106
リグニン・ヘミセルロース結合体のマイクロ波加熱
東　順一、土井美紀、越島哲夫

京都大学木材研究所
Microwave heating of lignin hemicellulose complex
Junichi Azuma, Miki Doi, Tetsuo Koshijima
Wood Research Institute, Kyoto University
Keywords: *Pinus densiflora,* MWL. LCC, furfural, sugars, ^{13}C-NMR, UV spectroscopy

1985-107
アルカリ蒸解において安定な LCC 結合について
種田英孝[*1]、細谷修二[*2]、中野準三[*1]
[*1] 東京大学農学部、[*2] 林業試験場
LCC bond stable during alkaline cooking
Hidetaka Taneda[*1], Shuji Hosoya[*2], Junzo Nakano[*1]
[*1]Faculty of Agriculture, the University of Tokyo, [*2]Forestry and Forest Products Research Institute
Keywords: guaiacylglycerol-α-methylglucoside-β-guaiacyl ether, HPLC, ^{13}C-NMR,

1985-108
アルカリ性処理におけるシリンギルグリセロール-β-シリンギルエーテル型モデル化合物の反応生成物について
堤　祐司、近藤隆一郎、今村博之
九州大学農学部
Reaction products from syringylglycerol-β-syringyl ether type model compounds on alkaline treatment
Yuji Tsutsumi, Ryuichiro Kondo, Hiroyuki Imamura
Faculty of Agriculture, Kyushu University
Keywords: soda cooking, kraft cooking, soda-AQ cooking, HPLC,

1985-109
β-*O*-4 型結合開裂の新反応
竹内寿一、坂井克己、文　星筆、今村博之
九州大学農学部
A new reaction for cleavage of β–□-4 type bonds
Jyuichi Takeuchi, Kokki Sakai, Sung-Phil Mung, Hiroyuki Imamura
Faculty of Agriculture, Kyushu University
Keywords: methanol, ethanol, isopropanol, *t*-butyl alcohol, magnesium sulfite, lignin

1985-110
有機溶媒と亜硫酸塩による脱リグニン（V） 低分子フェノール類について
文　星筆、坂井克己、今村博之
九州大学農学部
Delignification with organic solvents and sulfite (V), On the low molecular weight phenols
Sung-Phil Mung, Kokki Sakai, Hiroyuki Imamura
Keywords: *Cryptomeria japonica,* magnesium sulfite, phenols, isopropyl alcohol,

1985-111
フェニルクマラン型構造のオゾン分解について
羽生直人、松本雄二、中野準三
東京大学農学部
Ozonolysis of phenylcoumaran type structure
Naoto Habu, Yuji Matsumoto, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: dicarboxylic acids, GLC, GC-MS, ^{1}H-NMR

1985-112
ヨウ素化トリメチルシランによるリグニン・エーテル結合の選択的開裂について
飯塚堯介、近藤哲男、中野準三

東京大学農学部
Selective cleavage of ether linkage in lignin by trimethylsilyliodide
Gyosuke Meshitsuka, Tetsuo Kondo, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: *Betula maximowicziana,* MWL, guaiacylglycerol–β-guaiacyl ether, ^{1}H-NMR

1985-113
蒸煮処理材酵素糖化残渣リグニンの性状について
須藤賢一、志水一允、島田謹爾、桜井孝一、藤井智之
林業試験場
Characterization of residual lignin after steaming and enzymatic hydrolysis
Kenichi Sudo, Kazumasa Shimizu, Kinji Shimada, Koichi Sakurai, Tomoyuki Fujii
Forestry and Forest Products Research Institute
Keywords: *Betula platyphylla*, nitrobenzene oxidation, permanganate oxidation,

1985-114
Guaiacylglycerol−β−guaiacyl ether と lignin 生分解に関与する酵素について
沖　妙、石川久雄
愛媛大学農学部
Enzymes involved in the biodegradation of guaiacylglycerol−β−guaiacyl ether and lignin
Tae Oki, Hisao Ishikawa
Faculty of Agriculture, Ehime University
Ketwords: *Phanerochaete chrisosporium, Coprinus aff ellisii*, UV spectroscopy, GPC

1985-115
リグニン分解へのバイオミメティックアプローチ（IV) —鉄・ポルフイリン錯体と一電子酸化剤によるリグニン関連化合物の分解機構
島田幹夫[*1]、河波好宏[*2]、梅澤俊明[*1]、棚橋光彦[*1]、樋口隆昌[*1]、岡本　忠[*3]
[*1] 京都大学木材研究所、[*2] 近畿大学農学部、[*3] 京都大学化学研究所
Biomimetic approach to the biodegrdation of lignin (IV), -Degradation mechanism of lignin related compounds by ferriporphyrin and one electron oxidant
Mikio Shimada[*1], Yoshihiro Kawanami[*2], Toshiaki Umezawa[*1], Mitsuhiko Tanahashi[*1], Takayoshi Higuchi[*1], Tadashi Okamoto[*3]
[*1]Wood Research Institute, Kyoto University, [*2]Faculty of Agriculture, Kinki University, [*3]Institute for Chemical Research, Kyoto University
Keywords: active oxygen species, phenylcoumaran, heme-enzyme, t-buthylhydroperoxide, ceric ammonium nitrate

1985-116
カワラタケ菌体外酵素によるリグニンモデル化合物の分解
諸星紀幸、中村雅哉、原口隆英
東京農工大学農学部
Degradation of lignin model compounds by extracellular enzyme of *Coriolus versicolor*
Noriyuki Morohoshi, Masaya Nakamura, Takafusa Haraguchi
Faculty of Agriculture, Tokyo University of Agriculture and Technology
Keywords: laccase Ⅲ, guaiacylglycerol−β−guaiacyl ether, guaiacylglycerol−β−syringyl ether

1985-117
カワラタケラッカーゼによる β-1 型リグニンモデル化合物の分解
河合真吾[*1]、梅澤俊明[*1]、島田幹夫[*1]、樋口隆昌[*1]、小池一雄[*2]、西田友昭[*2]、諸星紀幸[*3]、原口隆英[*3]
[*1] 京都大学木材研究所、[*2] 王子製紙株式会社中央研究所、[*3] 東京農工大学農学部
Degradation of *β*-1 type lignin model compounds by laccase of *Coriolus versicolor*
Shingo Kawai[*1], Toshiaki Umezawa[*1], Mikio Shimada[*1] Takayoshi Higuchi[*1], Kazuo Koike[*2], Tomoaki Nishida[*2], Noriyuki Morohoshi[*3], Takafusa Haraguchi[*3]

^{*1}Wood Research Institute, Kyoto University, ^{*2}Oji Paper Co. Ltd., ^{*3} Faculty of Agriculture, Tokyo University of Agriculture and Technology.
Keywords: biodegradation, lignin substructure model compound, stable isotope tracer, $^{18}O_2$, mass spectrometry, 1,2-disyringylpropane-1,3-diol

1985-118
特別講演、酵母細胞壁溶解酵素とその利用
高知大学農学部
長崎　亀
Invited lecture ; Enzymes involved in the dissolution of yeast cell wall and its utilization
Susumu Nagasaki
Faculty of Agriculture, Kochi University
Keywords: β-1,3 glucanase,

1985-201
Phanerochaete chrysosporium による β-*O*-4 二量体の分解における*β*-アリール基の転位と Cα−Cβ 開裂
梅澤俊明、樋口隆昌
京都大学木材研究所
Rearrangement of β-aryl group and Cα−Cβcleavage in the degradation of β-*O*-4 dimer by *Phanerochaete chrysosporium*
Toshiaki Umezawa, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: ^{2}H, ^{13}C, ^{18}O, stable isotope tracer method, ^{1}H-NMR, mass spectrometry

1985-202
シュードモナス属細菌 TMY1009 株の変異株による β-エーテル型モデル化合物の分解と中間代謝物の生成
安部修一、鮫島正浩、佐分義正、善本知孝
東京大学農学部
Degradation of β-*O*-4 type lignin model compounds and formation of intermediate metabolites by the mutant of *Pseudomonas* TMY1009
Shuichi Abe, Masahiro Samejima, Yoshimasa Saburi, Tomotaka Yoshimoto
Faculty of Agriculture, the University of Tokyo
Keywords: β-*O*-4, TLC, UV spectroscopy

1985-203
好アルカリ性細菌によるリグニンモデル化合物及びリグニンの分解
川上日出国、青井理恵、丹羽　淳
名古屋大学農学部
Degradation of lignin model compounds and lignin by alkalophilic bacteria
Hidekuni Kawakami, Rie Aoi, Makoto Niwa
Faculty of Agriculture, Nagoya University
Keywords: diarylpropane diol, beech, *Fagus crenata,* 1,2-guaiacylpropane-1,3-diol, 1-guaiacyl-2-syringylpropane GPC

1985-204
白色腐朽菌 *Phanerochaete chrysosporium* の生分解によって生成した脱脂シラカンバチップ中の低分子成分
寺沢　実[*1]、香山　彊[*1]、C.L. Chen[*2], D.-S. Tai[*3]
北海道大学農学部、ノースカロライナ州立大学、南京林学院
Low molecular weight compounds formed in the degradation of extractive-free birch tips by a white rot fungus *Phanerochaete chrysosporium*
Minoru Terasawa[*1], Tsutomu Kayama[*1] C.L. Chen[*2], D.-S. Tai[*3]
[*1]Faculty of Agriculture, Hokkaido University, [*2]North Carolina State University, [*3]Nanjin Forestry University
Keywords: *Betula platyphylla,* acetophenone derivatives, ligninase

1985-205
ミツマタ靭皮の酵素パルプ化過程におけるリグニン及びヘミセルロースの溶出挙動
田辺寛之、小林良生
四国工業技術試験所
Dissolution behavior of lignin and hemicellulose during enzymatic pulping of mitsumata (oriental paperbush) bast
Hiroyuki Tanabe, Yoshinari Kobayashi
Government Industrial Research Institute, Shikoku
Keywords: *Edgeworthia chrysantha,* carbohydrate composition

1985-206
菌処理マニラ麻の H_2O_2 添加 TMP 化
赤松 勲、上嶋 洋、吉原一年
四国工業技術試験所
Preparation of thermomechanical pulp with addition of hydrogen peroxide from fungi treated Manila hemp
Isao Akamatsu, Hiroshi Kamishima, Kazutoshi Yoshihara
Government Industrial Research Institute, Shikoku
Keywords: *Coriolus hirtus,* Klason lignin, holocellulose, pulp yield, pulp properties

1985-207
GP リグニン中のコニフェリルアルデヒド構造の挙動について
平嶋英則、住本昌之
九州大学農学部
Behaviors of coniferyl aldehyde structure in GP lignin
Hidenori Hirashima, Masashi Sumimoto
Faculty of Agriculture, Kyushu University
Keywords: red pine, *Pinus densiflora,* H_2O_2, $NaBH_4$

1985-208
リグノセルロースの HF 糖化 —HF リグニンの構造
広居忠量、石井 忠
林業試験場
Saccharification of lignocellulose by HF, -Structure of HF lignin
Tadakazu Hiroi, Tadashi Ishii
Forestry and Forest Products Research Institute
Keywords: red pine, *Pinus densiflora,* white birch, *Betula platyphylla,* ^{13}C-NMR, IR spectroscopy, permanganate oxidation

1985-209
広葉樹材蒸煮処理効果の樹種による差
山口 彰、 志水一允、桜井孝一、藤井智之
林業試験場
Differences in the effectiveness of steaming for saccharification among wood species
Akira Yamaguchi, Kazumasa Shimizu, Koichi Sakurai, Tomoyuki Fujii
Forestry and Forest Products Research Institute
Keywords: enzymatic susceptibility, nitrobenzene oxidtion, S/V ratio, sugar composition

1985-210
リグニンの繊維化について
須藤賢一、志水一允
林業試験場
Preparation of fiber from lignin
Kenichi Sudo, Kazumasa Shimizu
Forestry and Forest Products Research Institute

Keywords: carbon fiber, white birch, *Betula platyphylla,* steaming, methanol extraction

1985-211
The Effect of Modified Lignosulphonate on Beating
Kalle Levon, Gyosuke Meshitsuka and Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: aminated lignosulphonate, mannich reaction, beating rate, freeness,

1985-212
リグニンの水素化分解 —反応温度および時間の検討—
小山 実、金沢健治、山田谷正子、杉本義一
化学技術研究所
Hydrogenolysis of lignin. -Investigation of reaction time and temperature
Makoto Koyama, Kenji Kanazawa, Masako Yamadaya, Giichi Sugimoto
National Chemical Laboratory for Industry
Keywords: thiolignin, cresol lignin, molecular weight distribution, monophenols,

1985-213
無機吸着剤に濃縮したバイオマスの熱分解
猪狩俶将[*1]、横山正一郎[*1]、井上晴彦[*2]
[*1] 化学技術研究所, [*2] クニミネ工業株式会社
Pyrolysis of biomass adsorbed on inorganic adsorbents
Yoshimasa Ikari[*1], Shoichiro Yokoyama[*1], * Haruhiko Inoue[*2]
[*1]National Chemical Laboratory for Industry, [*2]Kunimine Industries Co. Ltd.
Keywords: gasification, methanol synthesis, recovery of adsorbent

1985-214
ソルボリシスパルプ化による木材の脱リグニン —パルプ化条件とリグニンの性質
佐野 嘉拓、笹谷 宜志
北海道大学農学部
Delignification of wood by solvolysis pulping, -Pulping conditions and the properties of lignin
Yoshihiro Sano, Takashi Sasaya
Faculty of Agriculture, Hokkaido University
Keywords: beech, *Fagus crenata,* white birch, *Betula platyphylla,* cresol, solvolysis lignin

1985-215
ソルボリシスパルプ化による木材の脱リグニン —パルプ残存リグニン
枝重有祐、佐野嘉拓、笹谷宜志
北海道大学農学部
Delignification of wood by solvolysis pulping, -Residual lignin in pulp
Yusuke Edashige, Yoshihiro Sano, Takashi Sasaya
Faculty of Agriculture, Hokkaido University
Keywords: beech, *Fagus crenata,* cresol, gel filtration, MWL, nitrobenzene oxidation, ^{1}H-NMR

1985-216
クレゾールを含むヘミセルロース水溶液の精製
西山昌史、細川 純、上嶋 洋
四国工業技術試験所
Removal of cresol from aqueous hemicellulose and cresol solution
Masashi Nishiyama, Jun Hosokawa, Hiroshi Kamishima
Government Industrial Research Institute, Shikoku
Keywords: beech, *Fagus crenata,* solvolysis pulping, cresol, hemicellulose

1985-217
古代紙の打紙について

大川昭典[*1]、増田勝彦[*2]
[*1] 高知県紙業試験場、[*2] 東京国立文化財研究所

Beating of ancient paper

Akinori Ohkawa[*1], Katsuhiko Masuda[*2]
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Keywords: ancient paper, beating, breaking length

1985-218

特別講演、リグニン研究の回顧

中野準三
東京大学農学部

Invited lecture; A review of my lignin research

Junzo Nakano
Faculty of Agriculture, the University of Tokyo

第31回（1986.10.21-22）京大会館

1986-101
トドマツ圧縮あて材仮道管の木化
高部圭司、深沢和三
北海道大学農学部
Lignification of the tracheid of todomatsu compression wood
Keiji Takabe, Kazumi Fukazawa
Faculty of Agriculture, Hokkaido University
Keywords: *Abies Mayriana,* UV microscope, electron microscope, peroxidase activity

1986-102
カラマツ樹皮のファイバースクレレイドの機械的単離とその化学成分
竹田昌文、寺沢　実、香山　彊
北海道大学農学部
Mechanical isolation and chemical components of Japanese larch fiber sclereid
Masafumi Takeda, Minoru Terasawa, Tsutomu Kayama
Faculty of Agriculture, Hokkaido University
Keywords: UV microscope, thioacidolysis, MWL,

1986-103
広葉樹新生組織中のリグニンの性状（II）
厳　泰振、飯塚堯介、石津　敦、中野準三
東京大学農学部
Characterization of lignin in differentiating xylem of hardwood (II)
Tae Jin Eom, Gyosuke Meshitsuka, Atsushi Ishizu, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: *Betula maximowicziana,* MWL, LCC, ^{1}H-NMR, nitrobenzene oxidation

1986-104
アカマツリグニン・糖結合体の糖鎖とリグニンの結合位置について
渡辺隆司、海津澄子、越島哲夫
京都大学木材研究所
Bonding position between carbohydrate and lignin in red pine LCC
Takashi Watanabe, Sumiko Kaizu, Tetsuo Koshijima
Wood Research Institute, Kyoto University
Keywords: *Pinus densiflora,* DDQ oxidation, cellulase,

1986-105
ブナのリグニン・ヘミセルロース結合体におけるリグニンと糖の結合様式について
東　順一[*1]、越島哲夫[*2]
[*1] 京都大学農学部、[*2] 京都大学木材研究所
Linkages between lignin and carbohydrate in beech lignin carbohydrate complex
Junichi Azuma[*1], Tetsuo Koshijima[*2]
[*1]Faculty of Agriculture, Kyoto University, [*2]Wood Research Institute, Kyoto University
Keywords: *Fagus crenata,* DDQ oxidation, ^{13}C-NMR,

1986-106
木材腐朽菌によるリグニンモデル配糖体の生成について
近藤隆一郎、今村博之
九州大学農学部
Formation of glycoside of lignin model compounds by wood rotting fungi
Ryuichiro Kondo, Hiroyuki Imamura
Faculty of Agriculture, Kyushu University

Keywords: *Polyporus versicolor, Tyromyces palustris*, β−glucosidase, laccase

1986-107
好アルカリ性細菌による水溶性リグニンの生成
川上日出国、丹羽　淳
名古屋大学農学部
Formation of water-soluble lignin by alkalophilic bacteria
Hidekuni Kawakami, Makoto Niwa
Faculty of Agriculture, Nagoya University
Keywords: lignin degradation, wheat, *Hordeum vulgare*, poplar, *Populus* sp.,

1986-108
白色腐朽菌マイタケによる木材からの選択的脱リグニン
広居忠量、藤井智之
林業試験場
Selective delignification of wood by white rot fungus *Grifora frondosa*
Tadakazu Hiroi, Tomoyuki Fujii
Forestry and Forest Products Research Institute
Keywords: *Betula platyphylla,* microscopy, compound middle lamella, secondary wall

1986-109
α位にケトンを有するβ-*O*-4型ジリグノールの*Fusarium solani* M-13-1による分解と立体選択的還元（第2報）
片山健至[*1]、十河村男[*1]、堀池満子[*1]、三木敬夫[*1]、小橋啓志[*1]、樋口隆昌[*2]
[*1]香川大学農学部、[*2]京都大学木材研究所
Degradation and stereoselective reduction of β-*O*-4 dilignol with a-ketone group by *Fusarium solani* M-13-1 (II)
Takeshi Katayama[*1], Murao Sogo[*1], Mitchiko Horiike[*1], Takao Miki, [*1] Keishi Kohashi[*1], Takayoshi Higuchi[*2]
[*1]Faculty of Agriculture, Kagawa University, [*2]Wood Research Institute, Kyoto University
Keywords: *erythro*/*threo* ratio, ^{1}H-NMR, syringylpropanone, UV spectroscopy

1986-110
カワラタケラッカーゼの単離とその化学的、生化学的特徴
諸星紀幸、吉武彰文、片山義博、原口隆英
東京農工大学農学部
Isolation of laccase fom *Coriolus versicolor*, and its chemical and biochemical characteristics
Noriyuki Morohoshi, Akifumi Yoshitake, Yoshihiro Katayama, Takafusa Haraguchi
Faculty of Agriculture, Tokyo University of Agiculture and Technology
Keywords: phenol oxidase, electrophoresis, crystallization, antigen

1986-111
Lignin peroxidaseによるβ-*O*-4リグニンモデル化合他の分解
三木啓司[*1]、Michael H. Gold[*2]
[*1]公害資源研究所、[*2]Oregon Graduate Center
Degradation ofβ-*O*-4 type lignin model compounds by lignin peroxidase
Keiji Miki[*1], Michael H. Gold[*2]
[*1]National Research Institute for Pollution and Resources, [*2]Oregon Graduate Center
Keywords: *Phanerochaete chrysosporium*, cation radical, ^{18}O tracer,

1986-112
酵素によるジオキサンリグニンの生分解
沖　妙、石川久雄
愛媛大学農学部
Biodegradation of dioxane lignin by enzyme

Tae Oki, Hisao Ishikawa
Faculty of Agriculture, Ehime University
Keywords: *Phanerochaete chrysosporium,* dioxane lignin, nitrobenzene oxidation

1986-113
リグニンモデル化合物分解酵素遺伝子のクローニング（I）大腸菌−*Pseudomonas* シャトルベクターpKT230 およびコスミドベクターpVK100 の受動的伝達能力を利用した分解酵素遺伝子のクローニング系の確立
片山義博[*1]、西川誠司[*1]、諸星紀幸[*1]、原口隆英[*1]、山崎眞狩[*2]
[*1] 東京農工大学農学部、[*2] 東京大学農学部
Cloning of the genes related to the enzyme for lignin model compound degradation, I. -Constrution of the cloning system using the *Escherichia coli* and *Pseudomonas* spp. shuttle vector pKT230 and cosmid vector pVK100 by transconjugation
Yoshihiro Katayama[*1], Seiji Nishikawa[*1] Noriyuki Morohoshi[*1], Takafusa Haraguchi[*1], Makari Yamasaki[*2]
[*1]Faculty of Agriculture, Tokyo University of Agriculture and Technology, [*2]Faculty of Agriculture , the University of Tokyo
Keywords: 5,5-dehydrodivanillic acid, protocatechuic acid, ferulic acid

1986-114
リグニンモデル化合物分解酵素遺伝子のクローニング（II）受動的伝達能力を有する大腸菌−*Pseudomonas* シャトルベクターpKT230 を用いた *P. paucimobilis* SYK-6 株のジーンライブラリの構築とクローニング
西川誠司[*1]、片山義博[*1]、中村雅哉[*1]、村山彰啓[*1]、諸星紀幸[*1]、原口隆英[*1]、山崎眞狩[*2]
[*1] 東京農工大学農学部、[*2] 東京大学農学部
Cloning of the genes related to the enzyme for lignin model compound degradation (II), -Construction of gene library from *Pseudomonas paucimobilis* SYK-6 with the shuttle vector pKT230 by transconjugation
Seiji Nishikawa[*1], Yoshihiro Katayama[*1], Masaya Nakamura[*1], Akihiro Murayama[*1], Noriyuki Morohoshi[*1], Takafusa Haraguchi[*1], * Makari Yamasaki[*2]
[*1]Faculty of Agriculture, Tokyo University of Agriculture and Technology, [*2]Faculty of Agriculture , the University of Tokyo
Keywords: *Pseudomonas putida*, vanillic acid, protocatechuic acid,

1986-115
Ulin 材（*Eusideroxylon zwageri*）の耐朽性と化学成分
Wasrin Syafii、善本知孝、鮫島正浩
東京大学農学部
Durability and chemical components of Ulin (*Eusideroxylon zwageri*) wood
Wasrin Syafii, Tomotaka Yoshimoto, Masahiro Samejima
Faculty of Agriculture, the University of Tokyo
Keywords: *Coriolus vercicolor, Tyromeces polutris*, decay test, eusiderin, neolignans

1986-116
菌処理マニラ麻の H_2O_2 添加 TMP 化（その 2）
赤松　勲、上嶋　洋、吉原一年
四国工業技術試験所
Thermomechanical pulping of fungi treated Manila hemp by addition of H_2O_2 (II)
Susumu Akamatsu, Hiroshi Kamishima, Kazutoshi Yoshihara
Government Industrial Research Institute, Shikoku
Keywords: *Coriolus hirstus*, brightness

1986-117
白色腐朽菌によるパルプ漂白排水の脱色・脱塩素
松本雄二[*1]、Hou-min Chang[*2], T. Joyce[*2], T. K. Kirk[*3]
[*1] 東京大学農学部、[*2] ノースカロライナ州立大学、[*3] 米国林産物研究所
Decoloration and dechlorination of pulp bleach effluent by white rot fungi
Yuji Matsumoto[*1], Hou-min Chang[*2], T. Joyce[*2], T. K. Kirk[*3]

[*1]Faculty of Agriculture, the University of Tokyo, [*2]North Carolina State University, [*3]Forest Products Laboratory, USDA
Keywords: *Phanerochaete chrysosporium*, rotating biological contactor,

1986-118
パルプ廃液処理に関する研究（5） 廃液リグニンおよびフェノールモノマー類の担子菌類による処理性
鮫島一彦、谷岡俊彦、高村憲男
高知大学農学部
Studies on treatment of pulp effluent (V), Treatability of effluent lignin and phenol monomer by basidiomycetes
Kazuhiko Sameshima, Toshihiko Tanioka, Norio Takamura
Keywords: *Polystictus versicolor, Pleurotus ostreatus* , vanillyl alcohol, vanillin, vanillic acid

1986-119
特別講演、人工チトクロム P–450 を用いる脂肪族・芳香族化合物の酸化
田伏岩夫
京都大学工学部
Invited lecture ; Oxidation of aliphatic and aromatic compounds by artificial cytochrome P-450
Iwao Tabushi
Faculty of Engineering, Kyoto University

1986-201
亜硫酸ナトリウム、ホルムアルデヒドおよびキノン化合物を用いた新蒸解法
大井　洋、中野準三、石津　敦
東京大学農学部
New pulping process with sodium sulfite, formaldehyde and quinone compounds
Hiroshi Ohi, Junzo Nakano, Atsushi Ishizu
Faculty of Agriculture, the University of Tokyo
Keywords: yezo spruce, *Picea jezoensis*. beech, *Fagus crenata*, saghalien fir, *Abies Mayriana*,
1986-202
有機溶媒と亜硫酸塩による脱リグニン（VII）パルプ品質の改善について
文　星筆、坂井克己、今村博之
九州大学農学部
Delignification with organic solvents and sulfite (VII), Improvement of pulp properties
Sung-Phil Mung, Kokki Sakai, Hiroyuki Imamura
Faculty of Agriculture, Kyushu University
Keywords: *Pinus rigida*×*Pinus taeda*, *Betula platyphylla,* isopropyl alcohol, secondary butyl alcohol

1986-203
フェノオルガノソルブパルプ化法（第 3 報）
高橋昭博、佐野嘉拓、笹谷宜志
北海道大学農学部
Phenorganosolv pulping (III)
Akihiro Takahashi, Yoshihiro Sano, Takashi Sasaya
Faculty of Agriculture, Hokkaido Univeersity
Keywords: *Fagus crenata,* pulping, *n*-propyl alcohol, phenol, cresol, pyrocatechol, dissolved lignin

1986-204
有機酸蒸解におけるリグニンの挙動
安田征市、伊藤範明
名古屋大学農学部
Behavior of lignin during pulping with organic acids
Seiichi Yasuda, Noriaki Ito
Faculty of Agriculture, Nagoya University
Keywords: solvolysis pulping, lignin model compound, acetic acid, arylglycerol-β–aryl ether

1986-205
酢酸パルプ化における脱リグニン反応
J. L. Davis[*1]、中坪文明[*1]、村上浩二[*1]、R. A. Young[*2]
[*1] 京都大学農学部、[*2]University of Wisconsin
Delignification reaction during acetic acid pulping
J. L. Davis[*1], Fumiaki Nakatsubo[*1], Koji Murakami[*1], R. A. Young[*2]
[*1]Faculty of Agriculture, Kyoto University, [*2]University of Wisconsin
Keywords: guaiacylglycerol-β-guaiacyl ether, enol ether, Hibbert's ketones

1986-206
オゾン分解によるリグニン化学構造の研究 —β-5、β-1 型構造に由来する二塩基性酸の検索
羽生直人、松本雄二、石津　敦、中野準三
東京大学農学部
Structural study of lignin by ozonolysis. - Investigation of dicarboxylic acids derived from β-5 and β-1 structures
Naoto Habu, Yuji Matsumoto, Atsushi Ishizu, Junzo Nakano
Faculty of Agriculture, the University of Tokyo
Keywords: dihydrodehydrodiconiferyl alcohol, GLC, GC-MS, ^{13}C-NMR

1986-207
リグニンのメカノケミストリー — モデル化合物のメカノケミカル反応について
李　典艶、橘　燦郎、住本昌之
九州大学農学部
Mechanochemistry of lignin, -Mechanochemical reaction of lignin model compounds
Dian Yan Lee, Sanro Tachibana, Masashi Sumimoto
Faculty of Agriculture, Kyushu University
Keywords: coniferyl alcohol methyl ether, veratrylglycerol-*β*-aryl ether, GLC, MS

1986-208
A study on mechanism of pyrolized lignin
Wenda Lu, Jian Li, Sheng Luo Gwei, Yu Koh ming
Northeast Forestry University, China
Keywords: *Larix dahurica,* dioxane lignin, DSC, IR

1986-209
針葉樹材酵素糖化のためのオゾン酸化前処理
林　徳子、細谷修二、志水一允
林業試験場
Ozonation pretreatment for the enzymatic hydrolysis of softwood
Noriko Hayashi, Shuji Hosoya, Kazumasa Shimizu
Forestry and Forest Products Research Institute
Keywords: *Cryptomeria japonica*, polarization microscope, cell wall morphology

1986-210
酸糖化リグニンのラジカルスルホン化
渡辺正介、飯塚堯介、石津　敦、中野準三
東京大学農学部
Radical sulphonation of acid hydrolysis lignin
Shosuke Watanabe, Gyosuke Meshitsuka, Atsushi Ishizu, Junzo Nakano
Faculty of Agriculture, The University of Tpkyo
Keywords: *Betula maximowicziana*, sodium sulfite, MWL, IR

1986-211

リグニン系高分子電解質と水との相互作用
畠山兵衛[*1]、岩田ひろ[*2]、中村邦雄[*3]、畠山立子[*4]
[*1] 製品科学研究所、[*2] 日本紙パルプ研究所, [*3] 神奈川県工業試験所、[*4] 繊維高分子材料研究所
Interaction between water and polyelectrolyte derived from lignin
Hyoe Hatakeyama[*1], Hiro Iwata[*2], Kunio Nakamura[*3], Tatsuko Hatakeyama[*4]
[*1]Industrial Products Research Institute, [*2]Japan Pulp & Paper Research Institute, Inc., [*3]Kanagawa Industrial Technology Center, [*4]Institute for Textiles and Polymers
Keywords: sodium lignosulfonate, DSC, NMR, relaxation time

1986-212
リグニン分解物を原料とする耐熱性高分子
広瀬重雄[*1]、畠山兵衛[*1]、中村邦雄[*2]、畠山立子[*3]
[*1] 製品科学研究所、[*2] 神奈川県工業試験所、[*3] 繊維高分子材料研究所
Heat resistant polymer prepared from lignin degradation products
Shigeo Hirose[*1], Hyoe Hatakeyama[*1], Kunio Nakamura[*2], Tatsuko Hatakeyama[*3]
[*1]Industrial Products Research Institute, [*2]Kanagawa Industrial Technology Center, [*3]Institute for Textiles and Polymers
Keywords: polyester, DSC, X ray analysis, Tg

1986-213
リグニンの水素化分解 —高温における反応時間の影響
小山 実、金沢健治、山田谷正子、杉本義一
化学技術研究所
Hydrogenolysis of lignin, -Effect of reaction time at high temperature
Makoto Koyama, Kenji Kanazawa, Masako Yamadaya, Giichi Sugimoto
National Chemical Laboratory for Industry
Keywords: cresol lignin, thiolignin, monophenols

1986-214
リグニン水素化分解生成物の質量分析 —分子イオンスペクトル法および MS-MS によるキャラクタリゼーション
杉本義一、石川啓一郎、丹羽吉夫、山田谷正子、金沢健治、小山 実
化学技術研究所
Mass spectrometric analysis of hydrogenolysis products of lignin, -Molecular ion spectral analysis and characterization by MS-MS analysis
Giichi Sugimoto, Keiichiro Ishikawa, Yoshio Niwa, Masako Yamadaya, Kenji Kanazawa, Makoto Koyama
National Chemical Laboratory for Industry
Keywords: thiolignin, alkylphenols

1986-215
フェノール類可溶化木材からの木材用接着剤
小野拡邦、須藤賢一、唐沢仁志
林業試験場
Wood adhesives from wood liquefied by phenol
Hirokuni Ono, Kenichi Sudo, Hitoshi Karasawa
Forestry and Forest Products Research Institute
Keywords: resol formaldehyde resin, GPC, torsional blade analysis

1986-216
リグニン系炭素繊維 —紡糸用リグニンの性状について
須藤賢一、志水一允
林業試験場
Lignin derived carbon fiber, —Properties of lignin suitable for spinning
Kenichi Sudo, Kazumasa Shimizu

Forestry and Forest Products Research Institute

Keywords: *Betula platyphylla,* hydrocracking, GPC, ^{1}H-NMR, ^{13}C-NMR, heat treatment, SEM

1986-217

爆砕リグニンの抗変異原性（第 2 報） —爆砕リグニン成分及び関連化合物について—

矢澤　到[*1]、野澤美津子[*1]、柿島　博[*1]、西島　靖[*1]、棚橋光彦[*2]、樋口隆昌[*2]
[*1] 鐘紡化粧品研究所、[*2] 京都大学木材研究所

Antimutagenicity of steam explosion lignin (II), Steam explosion lignin and related compounds

Toru Yazawa[*1], Mitsuko Nozawa[*1], Hiroshi Kakishima[*1], Yasushi Nishijima[*1], Mitsuhiko Tanahashi[*2], Takayoshi Higuchi[*2]
[*1]Research Laboratory, Kanebo Cosmetic Inc., [*2]Wood Research Institute, Kyoto University

Keywords: *Chamaecyparis obtuse, Betula platyphylla, Salmonella typhimurium*, coniferyl alcohol, peroxidase

1986-218

特別講演、リグニンの形成と構造の不均一性

寺島典二
名古屋大学農学部

Invited lecture: Heterogeneity in formation and structure of lignin

Noritsugu Terashima
Faculty of Agriculture, Nagoya University

Keywords: protolignin, condensed unit, *p*-hydroxyphenyl lignin, guaiacyl lignin, syringyl lignin, softwood, hardwood, microautoradiography, cell wall layers

第32回（1987.10.20-21）福岡リーセントホテル

1987-101

紫外線顕微分光法による広葉樹木部構成要素の木化過程の検討

高部圭司[*1]、深沢和三[*1]、寺島典二[*2]、福島和彦[*2]

[*1] 北海道大学農学部、[*2] 名古屋大学農学部

Studies on the lignification process of hardwood xylem elements by UV microscope

Keiji Takabe[*1], Kazumi Fukazawa[*1], Noritsugu Terashima[*2], Kazuhiko Fukushima[*2]

[*1]Faculty of Agriculture, Hokkaido University, [*2]Faculty of Agriculture, Nagoya University

Keywords: Oxford poplar, *Populus Maximowiczii*×*Populus berolinensis*, *Magnolia kobus*, cell wall layers

1987-102

木部細胞分化過程における各種成分量の変化 —切片のデンシトメトリー解析を中心として—

藤田 稔、杉山由美子、佐伯 浩

京都大学農学部

Changes of the amount of chemical components during differentiation of xylem cell, - Observation of sections by densitometry

Minoru Fujita, Yumiko Sugiyama, Hiroshi Saiki

Faculty of Agriculture, Kyoto University

Keywords: *Cryptomeria japonica, Chamaecyparis obtuse, Pinus Thunbergii, Robinia pseudoacacia,* proteins, peroxidase, lignin

1987-103

西洋ワサビペルオキシターゼを用いた免疫電顕観察法のモデル実験

杉山由美子、藤田 稔、佐伯 浩

京都大学農学部

Model experiment for immunoelectron microscopy by use of horseradish peroxidase

Yumiko Sugiyama, Minoru Fujita, Hiroshi Saiki

Faculty of Agriculture, Kyoto University

Keywords: *Armoracia rusticana,* diaminobenzidine, immunostaining, immunohistochemistry

1987-104

ミクロオートラジオグラフ法による広葉樹リグニン形成過程の可視化

福島和彦、寺島典二

名古屋大学農学部

Visualization of formation process of hardwood lignin by microautoradiography

Kazuhiko Fukushima, Noritsugu Terashima

Faculty of Agriculture, Nagoya University

Keywords: magnolia, *Magnolia kobus*, lilac, *Syringa vulgaris*, *p*-hydroxyphenyl lignin, guaiacyl lignin, syringyl lignin,

1987-105

強冷摩砕法による MWL，LCC の調製について

福田忠徳、寺島典二

名古屋大学農学部

Preparation of MWL and LCC by milling under super cooling conditions

Tadanori Fukuda, Noritsugu Terashima

Faculty of Agriculture, Nagoya University

Keywords: black pine, *Pinus Thunbergii,* liquid nitrogen, UV spectroscopy, IR spectroscopy

1987-106

エポキシ樹脂包埋 MWL の紫外線顕微分光測光

藤井智之

林業試験場
UV microspectroscopic analysis of MWL embedded in epoxy resin
Tomoyuki Fujii
Forestry and Forest Products Research Institute
Keywords: beech, *Fagus crenata,* cell wall model,

1987-107
硫酸法によるリグニン定量における酸可溶性リグニン量の評価
前川英一、一澤泰三、越島哲夫
京都大学木材研究所
Evaluation of acid soluble lignin in sulfuric acid lignin determination
Eiichi Maekawa, Taizo Ichizawa, Tetsuo Koshijima
Wood Research Institute, Kyoto University
Keywords: *Fagus crenata*. *Acer pictum*, *Pinus densiflora*, *Phyllostachys pubescens*, Klason lignin

1987-108
リグニンモデル化合物芳香族炭素の化学シフトに及ばす置換基の影響
青山政和[*1]、H. Y. Hassi[*2], D. Tai[*3]、C. L. Chen[*4], J. S. Gratzl[*4]
[*1] 北海道立林産試験場、[*2]Metsaliiton Teollisuus OY、[*3] 南京林業大学、[*4] ノースカロライナ州立大学
Effect of substituent groups on the ^{13}C chemical shift of the aromatic carbons of lignin model compounds
Masakazu Aoyama[*1], H.Y. Hassi[*2], D. Tai[*3], C.L. Chen[*4], J.S. Gratzl[*4]
[*1]Hokkaido Forest Products Research Institute, [*2]Metsaliiton Teollisuus OY, [*3]Nanjin Forestry University, [*4]North Carolina State University
Keywords: ^{13}C-NMR, substituent chemical shift

1987-109
微生物によるリグニン分解（第 1 報）—高活性，高選択性リグニン分解菌の探索
西田友昭、樫野由憲、三村精男、高原義昌
神戸製鋼所生物学研究所
Lignin biodegradation by wood rot fungi (I) —Screening of highly active and highly selective lignin degrading fungi
Tomoaki Nishida, Yoshinori Kashino, Akio Mimura, Yoshimasa Takahara
Biotechnology Research Laboratory, Kobe Steel. Ltd.
Keywords: *Fagus crenata*, guaiacol, gallic acid, phenoloxidase activity, ligninolytic activity

1987-110
嫌気性バクテリアによるリグニンモデル化合物の分解
川上日出国、陳　巍、大宮邦雄、清水祥一
名古屋大学農学部
Degradation of lignin model compounds by anaerobic bacteria
Hidekuni Kawakami, Wei Chen, Kunio Oomiya, Shoichi Shimizu
Faculty of Agriculture, Nagoya University
Keywords: *Fusobacterium varium*, *Enterococcus faecium*, biphenyl, β-ether, phenylcoumaran

1987-111
シュードモナス属細菌 TMY1009 株から得られるリグニンモデル化合物脱水素酵素
羽生直人、鮫島正浩、佐分義正、善本知孝
東京大学農学部
Lignin model compound-dehydrogenation enzyme obtained from *Pseudomonas* TMY1009
Naoto Habu, Masahiro Samejima, Yoshimasa Saburi, Tomotaka Yoshimoto
Faculty of Agriculture, the University of Tokyo
Keywords: phenylcoumaran, NAD, NADH,

1987-112

ヒイロタケによるリグニン関連芳香族化合物の分解
早川敏雄[*1]、原口隆英[*1]、樫野由憲[*2]
[*1] 東京農工大学農学部、[*2] 神戸製鋼所
Degradation of aromatic compounds related to lignin by *Pycnoporus coccineus*
Toshio Hayakawa[*1], Takafusa Haraguchi[*2], Yoshinori Kashino[*2]
[*1]Faculty of Agriculture, Tokyo University of Agriculture and Technology, [*2]Kobe Steel. Ltd.
Keywords: biodegradation, protocatechuic acid, catechol, oxygenase, GC-MS

1987-113
リグニン分解に対する酵素特性
沖　妙、石川久雄
愛媛大学農学部
Characteristics of lignin degrading enzyme
Tae Oki, Hisao Ishikawa
Faculty of Agriculture, Ehime University
Ketwords: *Phanerochaete chrysosporium*, dioxane lignin, laccase, peroxidase

1987-114
Phanerochaete chrysosporium におけるリグニン分解酵素系 —Manganese peroxidase の作用機構—
割石博之、Micheal H. Gold
Oregon Graduate Center
Ligninolytic enzyme system in *Phanerochaete chrysosporium*, - Reaction mechanism of manganese peroxidase
Hiroyuki Wariishi, Michael H. Gold
Oregon Graduate Center
Keywords: EPR spectroscopy, ^{14}NO-MnP, ^{15}NO-MnP,

1987-115
Lignin peroxidase によるリグニンモデル化合物の芳香環開裂
三木啓司[*1]、近藤隆一郎[*2]、Michael H. Gold[*3]
[*1] 公害資源研究所, [*2] 九州大学農学部、[*3]Oregon Graduate Center
Cleavage of aromatic rings of lignin model compounds by lignin peroxidase
Keiji Miki[*1], Ryuichiro Kondo[*2], Michael H. Gold[*3]
[*1]National Research Institute for Pollution and Resources, [*2]Faculty of Agriculture, Kyushu University, [*3]Oregon Graduate Center
Keywords: ^{18}O tracer, arylglycerol-β–biphenyl ether,

1987-116
フェノール類を媒介とする非フェノール性リグニンモデル化合物のカワラタケラッカーゼによる分解
河合真吾、梅澤俊明、樋口隆昌
京都大学木材研究所
Degradation of non-phenolic lignin model compounds in the presence of phenols by laccase of *Coriolus versicolor*
Shingo Kawai, Toshiaki Umezawa, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: biodegradation, lignin substructure model compound, 1,2-bis-(3,4,5-trimethoxyphenyl)-propane-1,3-diol, , mediator, syringaldehyde, GC-MS

1987-117
β-*O*-4-β-*O*-4 型リグニンモデル三量体のリグニンペルオキシターゼによる分解
梅澤俊明、樋口隆昌
京都大学木材研究所
Degradation of β-*O*-4-β-*O*-4 type lignin model trimer by lignin peroxidase
Toshiaki Umezawa, Takayoshi Higuchi
Wood Research Institute, Kyoto University

Keywords: *Phanerochaete chrysosporium*, GC-MS,

1987-118
バイオミメティツクポルフイリン触媒によるリグニン芳香環モデル化合物の環開裂反応
服部武文、島田幹夫、梅澤俊明、樋口隆昌
京都大学木材研究所
Ring cleavage reaction of lignin model compound by biomimetic porphyrin catalyst
Takefumi Hattori, Mikio Shimada, Toshiaki Umezawa, Takayoshi Higuchi
Wood research Institute, Kyoto University
Keywords: 3,4-dimethoxybenzylalcohol, lignin peroxidase, ^{18}O tracer,

1987-119
特別講演、最近のタンニンの研究から
西岡五夫
九州大学薬学部
Invited lecture ; Recent advances in research on tannin
Itsuo Nishioka
Faculty of Pharmaceutical Science, Kyushu University
Keywords: *Quercus salicina*, *Camellia sinensis*, biological activity

1987-201
シュードモナス属細菌 TMY1009 株におけるリグニンモデル化合物分解酵素産生遺伝子のセルフクローニング系について
鮫島正浩、善本知孝
東京大学農学部
Self cloning system of the genes for the production of lignin model compounds degrading enzyme in *Pseudomonas* TMY1009
Masahiro Samejima, Tomotaka Yoshimoto
Faculty of Agriculture, the University of Tokyo
Keywords: plasmid, gene library

1987-202
カワラタケ酵素遺伝子のクローニング（II）—Laccase III 糖鎖機能解析と cDNA の合成—
中村雅哉[*1]、吉武彰文[*1]、片山義博[*1*2]、諸星紀幸[*1]、原口隆英[*1]、
[*1] 東京農工大学農学部, [*2] 神戸製鋼生物学研究所
Cloning of the genes for the enzyme of *Coriolus versicolor* (II) – Functional analysis of sugar chains of laccase Ⅲ and the synthesis of cDNA
Masaya Nakamura[*1], Akifumi Yoshitake[*1], * Yoshihiro Katayama[*2], Noriyuki Morohoshi[*1], Takafusa Haraguchi[*1]
[*1]Faculty of Agriculture, Tokyo University of Agriculture and Technology, [*2]Biotechnology Research Laboratory, Kobe Steel, Ltd.
Keywords: sugar chain function

1987-203
リグニンモデル化合物分解酵素遺伝子のクローニング V
西川誠司[*1]、片山義博[*1*2]、政井英二[*1]，諸星紀幸[*1]、原口隆英[*1]、山崎眞狩[*3]
[*1] 東京農工大学農学部、[*2] 神戸製鋼生物学研究所、[*3] 東京大学農学部
Cloning of the genes for the lignin model compounds degrading enzyme (V)
Seiji Nishikawa[*1], Yoshihiro Katayama[*2], Eiji Masai[*1], Noriyuki Morohoshi[*1], Takafusa Haraguchi[*1], Makari Yamasaki[*3]
[*1]Faculty of Agriculture,Tokyo University of Agriculture and Technology, [*2]Biotechnology Research Laboratory, Kobe Steel Co. Ltd, [*3]Faculty of Agriculture, the University of Tokyo
Keywords: *Pseudomonas paucimobilis, Pseudomonas putida*, gene library,

1987-204
白色腐朽菌によるE段漂白排液の脱色機構
桃原郁夫[*1]、渋谷往男[*1]、松本雄二[*1]、石津　敦[*1]、H.-m Chang[*2]
[*1] 東京大学農学部、[*2] ノースカロライナ州立大学
Decoloration mechanism of E stage bleach effluent by white rot fungi
Ikuo Momohara[*1], Sumio Shibuya[*1], Yuji Matsumoto[*1], Atsushi Ishizu[*1], H.-m Chang[*2]
[*1]Faculty of Agriculture, the University of Tokyo, [*2]North Carolina State University
Keywords: *Phanerochaete chrysosporium*, loblolly pine, *Pinus taeda*, quinone structure

1987-205
白色腐朽菌によるパルプ漂白排水の突然変異原性の変化
渋谷往男、桃原郁夫、松本雄二、石津　敦
東京大学農学部
Changes of mutagenicity of pulp bleach effluent by treatment with white rot fungi
Sumio Shibuya, Ikuo Momohara, Yuji Matsumoto, Atsushi Ishizu
Faculty of Agriculture, the University of Tokyo
Keywords: *Phanerochaete chrysosporium*, Ames test, softwood KP

1987-206
トリメチルヨードシランによるリグニン中のエーテル結合の選択的開裂
牧野重人、飯塚堯介、石津　敦
東京大学農学部
Selective cleavage of ether linkage in lignin by trimethylsilyl iodide
Shigeto Makino, Gyosuke Meshitsuka, Atsushi Ishizu
Faculty of Agriculture, the University of Tokyo
Keywords: *Betula maximowicziana*, *Larix Kaempferi, Picea jezoensis,* MWL, molecular weight distribution,

1987-207
リグニンモデル2量体の水素化分解
小山　実、金沢健治、杉本義一、山田谷正子
化学技術研究所
Hydrogenolysis of dimeric model compounds of lignin
Makoto Koyama, Kenji Kanazawa, Gi-ichi Sugimoto, Masako Yamadaya
National Chemical Laboratory for Industry
Keywords: diphenyl ether, diphenyl methane, dibenzyl, metal catalyst

1987-208
ソルボリシスによる針葉樹材の脱リグニン
佐野嘉拓、笹谷宜志
北海道大学農学部
Delignification of softwood by solvolysis
Yoshihiro Sano, Takashi Sasaya
Faculty of Agriculture, Hokkaido University
Keywords: *Abies Mayriana*, cresol water, delignification mechanism, guaiacylglycerol-β-guaiacyl ether, veratrylglycerol-β-guaiacyl ether, ^{1}H-NMR

1987-209
有機酸蒸解におけるリグニンの挙動　―フェニルクマランおよびジアリールプロパン構造の反応性
安田征市
名古屋大学農学部
Behavior of lignin during cooking in organic acids, ―Reactivity of phenylcoumaran and diarylpropane structures
Seiichi Yasuda

Faculty of Agriculture, Nagoya University
Keywords: acetic acid cooking, phenylcoumaran, diarylpropane

1987-210
蒸煮・爆砕前処理によるアカシア類の利用
勝部和則[*1]、嘉手苅幸男[*2]、志水一允[*3]、藤井智之[*3]、須藤賢一[*3]、長沢定男[*3]
[*1] 岩手バイオマス研究センター, [*2] 沖縄県林業試験所、[*3] 林業試験場
Utilization of *Acacia* by steam explosion pretreatment
Kazunori Katsube[*1], Yukio Kategaru[*2], Kazumasa Shimizu[*3], Tomoyuki Fujii[*3], Kenichi Sudo[*3], Sadao Nagasawa[*3]
[*1]Iwate Biomass Research Center, [*2]Okinawa Prefectural Forest Experiment Station, [*3]Forestry and Forest Products Research Institute
Keywords: enzymatic hydrolysis, sugar composition, lignin structure

1987-211
爆砕処理によるリグニンの分解機構の解明（II)
Myrtha Karina、棚橋光彦、樋口隆昌
京都大学木材研究所
Degradation mechanism of lignin during steam explosion treatment (II)
Myrtha Karina, Mitsuhiko Tanahashi, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: guaiacylglycerol-β-guaiacyl ether, veratrylglycerol-β-guaiacyl ether, ^{1}H-NMR, GC-MS

1987-212
未利用林産資源の酵素、微生物による変換利用(1)—前処理としてのアスプルンドパルプの製造と解析—
鮫島一彦[*1]、藤原新二[*1]、高村憲男[*1]、黒田健一[*2]
高知大学農学部、筑波大学農林工学系
Utilization of unused forest resources by conversion with enzyme and microorganism (I) -Preparation and analysis of Asplund pulp as a pretreatment
Kazuhiko Sameshima[*1], Shinji Fujiwara[*1], Norio Takamura[*1], Ken-ichi Kuroda[*2]
[*1]Faculty of Agriculture, Kochi University, [*2] Institute of Agricultural and Forest Engineering, University of Tsukuba
Keywords: *Betula platyphylla, Fagus crenata, Zelkova serrata, Cryptomeria japonica, Chamaecyparis obtuse, Pinus densiflora,* enzymatic susceptibility

1987-213
アルカリ性サルファイト・キノン蒸解におけるリグニンの挙動
大井 洋[*1]、石津 敦[*1]、中野準三[*2]
[*1] 東京大学農学部、[*2] 福井工業大学工学部
Behavior of lignin during alkaline sulfite-quinone pulping
Hiroshi Ohi[*1], Atsushi Ishizu[*1], Junzo Nakano[*2]
[*1]Faculty of Agriculture, the University of Tokyo, [*2]Faculty of Engineering, Fukui University of Technology
Keywords: *Picea jezoensis, Fagus crenata, Abies sachalinensis,* gel filtration chromatography

1987-214
N 材クラフト蒸解において最終脱リグニンを阻害する多糖について
松本雄二[*1]、石津 敦[*1]、H.-m. Chang[*2]
[*1] 東京大学農学部, [*2] ノースカロライナ州立大学
Studies on the polysaccharides preventing final delignification in kraft pulping of softwood
Yuji Matsumoto[*1], Atsushi Ishizu [*1], H.-m. Chang[*2]
[*1]Faculty of Agriculture, the University of Tokyo, [*2]North Carolina State University
Keywords: *Pinus taeda*, LCC, hemicellulose-consisting sugars

1987-215
A preliminary study on paper aging caused by light

Jian Li, Gwei Sheng Luo, Wenda Lu, Yu Koh Ming
Northeast Forestry University, China
Keywords: ESCA, FTIR, SEM

1987-216
リグノスルホン酸塩—水系のメゾフェーズ
畠山兵衛[*1]、広瀬重雄[*1]、畠山立子[*2]
[*1] 製品科学研究所、[*2] 繊維高分子研究所
Meso phase of lignosulfonate-water system
Hyoe Hatakeyama[*1], Shigeo Hirose[*1], Tatsuko Hatakeyama[*2]
[*1]Industrial Products Research Institute, [*2]Institute for Textiles and Polymers
Keywords: DSC, ^{1}H-NMR, polarization microscope

1987-217
リグニンから誘導される含リン型ポリウレタン
広瀬重雄[*1]、矢野彰一郎[*1]、畠山兵衛[*1]、畠山立子[*2]
[*1] 製品科学研究所、[*2] 繊維高分子材料研究所
Polyurethane including phosphor derived from lignin
Shigeo Hirose[*1], Shoichiro Yano[*1], Hyoe Hatakeyama[*1], Tatsuko Hatakeyama[*2]
[*1]Industrial Products Research Institute, [*2]Institute for Textiles and Polymers
Keywords: *Fagus crenata,* solvolysis lignin, TG, heat resistance

1987-218
フェノール化リグニンの木材接着剤への応用
小野拡邦[*1]、須藤賢一[*1]、唐沢仁志[*1]、姚 忻[*2]
[*1] 林業試験場, [*2] 黒竜江省林産工業研究所
Utilization of phenolated lignin to wood adhesives
Hirokuni Ono[*1], Kenichi Sudo[*1], Hitoshi Karasawa[*1], Yao Xin[*2]
[*1]Forestry and Forest Products Research Institute, [*2]Forest Products Research Institute of Heilongjiang Province
Keywords: *Betula platyphylla,* GPC, IR spectroscopy,

1987-219
特別講演、酸素及び過酸化物漂白におけるリグニンの挙動
石川久雄
愛媛大学農学部
Invited lecture ; Reactions of lignin during oxygen and peroxide bleaching
Hisao Ishikawa
Faculty of Agriculture, Ehime University
Keywords: active oxygen species

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1988-101
ポプラの分子育種に関する研究（1）リグニン形成能に関与するアイソペルオキシターゼの性質
諸星紀幸、西田謙吾、山田恵子、三国順子、片山義博、原口隆英
東京農工大学農学部
Molecular breeding of poplar (I), Characterization of isoperoxidase involved to lignification
Noriyuki Morohoshi, Kengo Nishida, Keiko Yamada, Junko Mikuni, Yoshihiro Katayama, Takafusa Haraguchi
Faculty of Agriculture, Tokyo University of Agriculture and Technology
Keywords: *Populus euroamericana*, isoelectric focusing, gel filtration chromatography

1988-102
ポプラの分子育種に関する研究（2）ポプラカルスの分化誘導と Ti プラスミド導入系の確立
片山義博、柳田恒一郎、諸星紀幸、原口隆英
Molecular breeding of poplar (II), Induction of poplar callus differentiation and establishment of Ti plasmid introduction system
Yoshihiro Katayama, Koichiro Yanagida, Noriyuki Morohoshi, Takafusa Haraguchi
Faculty of Agriculture, Tokyo University of Agriculture and Technology
Keywords: *Agrobacterium tumefacience*

1988-103
イネにおけるリグニンの形成と構造
何　蘭芳、寺島典二
名古屋大学農学部
Formation and structure of lignin in rice plants
Lanfang He, Noritsugu Terashima
Faculty of Agriculture, Nagoya University
Keywords: *Oryza sativa*, microautoradiography, *p*-hydroxyphenyl lignin, guaiacyl lignin, syringyl lignin, AQ-soda pulping

1988-104
p–ヒドロキシフェニルリグニンの性質について
福島和彦、寺島典二
名古屋大学農学部
Properties of *p*-hydroxyphenyl lignin
Kazuhiko Fukushima, Noritsugu Terashima
Faculty of Agriculture, Nagoya University
Keywords: *Pinus Thunbergii*, microautoradiography, compression wood, HPLC

1988-105
LCC 生合成時における糖加水分解酵素の関与について
迫　孝、飯森武志、近藤隆一郎、今村博之
九州大学農学部
Participation of carbohydrate hydrolyzing enzyme during biosynthesis of LCC
Takashi Sako, Takeshi Iimori, Ryuichiro Kondo, Hiroyuki Imamura
Faculty of Agriculture, Kyushu University
Keywords: cellobiose, β-glucosidase, transglycosylation, coniferyl alcohol, isoconiferin

1988-106
過ヨウ素酸リグニンの調製と性状
種田英孝、石津　敦
東京大学農学部
Preparation and characterization of periodate lignin
Hidetaka Taneda, Atsushi Ishizu

Faculty of Agriculture, the University of Tokyo
Keywords: *Picea jezoensis*, Smith degradation, sugar contents,

1988-107
凍結粉砕を利用した木材酵素糖化とリグニンの抽出について
渡辺隆司、吉村直子、越島哲夫
京都大学木材研究所
Enzymatic saccharification of wood and extraction of lignin using cryomilling
Takashi Watanabe, Naoko Yoshimura, Tetsuo Koshijima
Wood Research Institute, Kyoto University
Keywords: *Pinus densiflora*, *Fagus crenata*, ball milling, SEM,

1988-108
オゾン分解によるリグニン化学構造の研究　—ピノレジノール型構造の存在の検討—
松本雄二、南　一守、石津　敦
東京大学農学部
Structural study on lignin by ozonolysis, —Investigation of the presence of pinoresinol structures—
Yuji Matsumoto, Kazumori Minami, Atsushi Ishizu
Faculty of Agriculture, the University of Tokyo
Keywords: *Fagus crenata, Picea jezoensis, Eucalyptus,* MWL, ^{13}C-NMR

1988-109
トリメチルヨードシランによるリグニン中のエーテル結合の選択的開裂
牧野重人、飯塚堯介、石津　敦
東京大学農学部
Selective cleavage of ether linkages in lignin by trimethylsilyl iodide
Shigeto Makino, Gyosuke Meshitsuka, Atsushi Ishizu
Faculty of Agriculture, the University of Tokyo
Keywords: *Picea jezoensis,* MWL, molecular weight distribution

1988-110
Acetylbromide へのリグノセルロースの溶解　—反応機構とリグニンの UV スペクトル
飯山賢治^{*1}、Adrian F. A. Wallis^{*2}
^{*1} 東京大学農学部、^{*2}CSIRO, Australia
Dissolution of lignocellulose in acetylbromide, -Reaction mechanism and UV spectra of lignin—
Kenji Iiyama^{*1}, Adrian F.A. Wallis^{*2}
^{*1}Faculty of Agriculture, the University of Tokyo, ^{*2}CSIRO, Australia
Keywords: *Pinus radiata*, UV spectroscopy, lignin model compound, GPC

1988-111
酸および加熱処理過程におけるリグニンの縮合について
船岡正光、柴田真美、加古辰成、阿部　勲
三重大学生物資源学部
Condensation of lignin during acid and heat treatment
Masamitsu Funaoka, Mami Shibata, Tatsunari Kako, Isao Abe
Faculty of Bioresources, Mie University
Keywords: *Picea jezoensis, Pseudotsuga taxifolia,* nucleus exchange reaction, nitrobenzene oxidation

1988-112
クラフト蒸解過程における複合中間層および二次壁領域でのリグニンのフラグメンテーションと縮合
船岡正光^{*1}、Vincent L. Chiang^{*2}
^{*1} 三重大学生物資源学部、^{*2}Michigan Technological University
Fragmentation and condensation of lignin in middle lamella and secondary wall during kraft cooking
Masamitsu Funaoka^{*1}, Vincent L. Chiang^{*2}

[*1]Faculty of Bioresources, Mie University, [*2]Michigan Technological University
Keywords: *Pseudotsuga taxifolia,* nuclear exchange reaction, nitrobenzene oxidation, middle lamella, secondary wall

1988-113
爆砕処理によるリグニンの分解機構解明(IV)—シナピルアルコール DHP の合成と高圧水蒸気処理
棚橋光彦、Myrtha Karina、樋口隆昌
京都大学木材研究所
Degradation mechanism of lignin during steam explosion (IV), -Synthesis of sinapyl alcohol DHP and its treatment with high pressure steam
Mitsuhiko Tanahashi, Myrtha Karina, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: ^{1}H-NMR, ^{13}C-NMR, GC-MS, acidolysis, syringaresinol, radical reaction

1988-114
リグニンのメカノケミストリー(IV) —フェニルクマランモデル化合物のメカノケミカル反応と其の生成物の過酸化水素反応—
李典 艶、住本昌之
九州大学農学部
Mechanochemistry of lignin (IV), —Mechanochemical reaction of phenylcoumaran type model compounds, and reaction of the products with hydrogen peroxide—
Dian Yan Lee, Masashi Sumimoto
Faculty of Agriculture, Kyushu University
Keywords: stilbene, ^{1}H-NMR, UV spectroscopy, IR spectroscopy, mass spectrometry

1988-115
酸糖化リグニンのラジカルスルホン化
渡辺正介、飯塚堯介、石津　敦
東京大学農学部
Radical sulphonation of acid hydrolysis lignin
Masasuke Watanabe, Gyosuke Meshitsuka, Atsushi Ishizu
Faculty of Agriculture, the University of Tokyo
Keywords: *Betula maximowicziana,* sodium sulphite, UV spectroscopy, GPC

1988-116
分別クラフトリグニンのガラス転移
吉田博久[*1]、R. Mörck、K. Kringstad[*2]、畠山兵衛[*3]
[*1] 東京都立大学工学部、[*2]STFI、[*3] 製品科学研究所
Glass transition of fractionated kraft lignin
Hirohisa Yoshida[*1], R. Mörck[*2], K. Kringstad[*2], Hyoe Hatakeyama[*3]
[*1]Faculty of Engineering, Tokyo Metropolitan University, [*2]STFI, Sweden, [*3]Industrial Products Research Institute
Keywords: solubility parameter, polydispersity, molecular weight distribution

1988-117
ソルボリシスリグニンを原料とするポリウレタンの力学特性
中村邦雄[*1]、R. Mörck[*2]、A. Reimann[*2]、K. Kringstad[*2]、畠山兵衛[*3]
[*1] 大妻女子大学、[*2]STFI、[*3]製品科学研究所
Mechanical properties of polyurethane prepared from solvolysis lignin
Kunio Nakamura[*1], R. Mörck[*2], A. Reimann[*2], K. Kringstad[*2], Hyoe Hatakeyama[*3]
[*1]Otsuma Women's University, [*2]STFI, Sweden, [*3]Industrial Products Research Institute
Keywords: *Fagus crenata,* PEG

1988-118

特別講演、糖質の生産とその高度利用について
小林昭一
農林水産省食品総合研究所
Invited lecture ; Production of carbohydrates and their advanced utilization
Shoichi Kobayashi
National Food Research Institute, Ministry of Agriculture, Fishery and Forestry
Keywords: sucrose, chitin, fructan, starch, isomerase, maltoligosaccharide, cyclodextrin

1988-201
カルボニル化合物を助剤とする亜硫酸ソーダ・キノン蒸解
中野準三、宮崎重和、隈原文康
福井工業大学工学部
Sodium sulfite-quinone cooking with carbonyl compounds as additives
Junzo Nakano, Shigekazu Miyazaki, Fumiyasu Kumahara
Fukui University of Technology
Keywords: *Pinus densiflora*, *Betula maximowicziana,* 1,4-dihydro-9,10-dihydroxyanthracene, formaldehyde

1988-202
アルカリ性サルファイト・キノン蒸解の脱リグニン機構
大井 洋、石津 敦
東京大学農学部
Delignification mechanism of alkaline sulfite-quinone cooking
Hiroshi Ohi, Atsushi Ishizu
Faculty of Agriculture, the University of Tokyo
Keywords: *Picea jezoensis*, *Abies sachalinensis, Fagus crenata,* MWL, DDA, 1,4-dihydro-9,10-dihydroxyanthracene, cellulose, β-ether cleavage,

1988-203
ソルボリシスパルプ化に関する研究 (第4報) 蒸解溶媒と蒸解反応
岩田ひろ、可知省吾、荒木 廣、青柳哲夫
日本紙パルプ研究所
Studies on solvolysis pulping (IV), Composition of cooking solvent and cooking reaction
Hiro Iwata, Shogo Kachi, Hiroshi Araki, Tetsuo Aoyagi
Japan Pulp & Paper Research Institute, Inc.
Keywords: *Fagus crenata, Pinus Thunbergii,* cresol, bound solvent

1988-204
硫酸触媒による広葉樹材の常圧パルプ化（第 2 報）
島本 周、中村雅幸、佐野嘉柘
北海道大学農学部
Pulping of hardwood at atmospheric pressure with sulfuric acid as catalyst (II)
Shu Shimamoto, Masayuki Nakamura, Yoshihiro Sano
Faculty of Agriculture, Hokkaido University
Keywords: *Betula maximowicziana,* acetic acid, phenol, ^{1}H-NMR, GPC

1988-205
未利用植物資源の PA 法（過酸化水素-アルカリ法）によるパルプ化 —パルプ工業におけるショートサーキットはどこまで可能か—
御田昭雄
化学技術研究所
Pulping of unutilized plant resources by PA method (hydrogen peroxide-alkali), —How far the short circuit of pulp industry could be achieved—
Akio Mita

National Chemical Laboratory for Industry
Keywords:	used paper, recyling, non-wood pulp

1988-206
伝統的和紙製造法の化学的研究（2）—木灰の分析と木灰蒸煮処理—
鮫島一彦、藤原新二、堀江大介、高村憲男
高知大学農学部
Chemical characterization of traditional process of Japanese paper production, II. -Analysis of ash and pulping with ash
Kazuhiko Sameshima, Shinji Fujiwara, Daisuke Horie, Norio Takamura
Faculty of Agriculture, Kochi University
Keywords:	*Edgeworthia chrysantha, Broussonetia kazinoki* × *B. papyrifera*, Washi paper, ash

1988-特別講演
森林経営の展望
熊崎　実
森林総合研究所
Invited lecture ; A perspective on forest management
Minoru Kumazaki
Forestry and Forest Products Research Institute

1988-207
アラゲカワラタケの1核菌糸体の生理特性とリグニンの分解
吉原一年、上嶋　洋、西山昌史、赤松　勲
四国工業技術試験所
Physiological characteristics of monokariotic mycelia of *Coriolus hirsutus* IFO4917 and the degradation of lignin
Kazutoshi Yoshihara, Hiroshi Kamishima, Masashi Nishiyama, Isao Akamatsu
Government Industrial Research Institute ,Sikoku
Keywords:	*Populus* sp., liquid culture, β-glucosidase, CMCase, xylanase, laccase

1988-208
白色腐朽菌*Phanerochaete chrysosporium*のリグニンパーオキシダーゼ生産能についての遺伝的改良
桑原正章、麻田恭彦、打越正延、凌　楓、木村義雄、山本澄人
香川大学農学部
Genetic improvement of lignin peroxidase productivity of white rot fungus *Phanerochaete chrysosporium*
Masaaki Kuwahara, Yasuhiko Asada, Masanobu Uchikoshi, Ling Feng, Yoshio Kimura, Sumito Yamamoto
Faculty of Agriculture, Kagawa University
Keywords:	DNA, mutant, DEAE–Sepharose chromatography,

1988-209
好アルカリ性コリネバクテリウム。　ジリグノール分解株のプロトプラスト化及び再生
川上日出国、葛原憲康
名古屋大学農学部
Alkalophilic *Corynebacterium.*　Protoplast formation and regeneration of the dilignol degrading strain
Hidekuni Kawakami, Noriyasu Kuzuhara
Faculty of Agriculture, Nagoya University
Keywords:	lignin degradation, lignin model compound, vanillin, protoplast,

1988-210
リグニンモデル化合物分解酵素遺伝子のクローニング（VIII）—*Pseudomonas paucimobilis* SYK−6の
β−エーテル結合開裂酵素—
政井英司[*1]，片山義博[*1*2]、西川誠司[*1]、山崎眞狩[*3]、諸星紀幸[*1]、原口隆英[*1]
[*1] 東京農工大学農学部、[*2] 神戸製鋼生物学研究所、[*3] 東京大学農学部

Cloning of the genes for the lignin model compounds degrading enzyme. VIII. -β-Ether cleaving enzyme of *Pseudomonas paucimobilis* SYK−6
Eiji Masai[*1], Yoshihiro Katayama[*2], Seiji Nishikawa[*1], Makari Yamasaki[*3], Noriyuki Morohoshi[*1], Takafusa Haraguchi[*1]
[*1]Faculty of Agriculture,Tokyo University of Agriculture and Technology, [*2]Biotechnology Research Laboratory, Kobe Steel, Ltd, [*3]Faculty of Agriculture, the University of Tokyo
Keywords: umbelliferone ether, vanillin ether,

1988-211
電気パルスによるシュードモナス属細菌への遺伝子の導入
鮫島正浩、鴨田重裕、善本知孝
東京大学農学部
Introduction of the genes to *Pseudomonas* by electric pulse
Masahiro Samejima, Shigehiro Kamota, Tomotaka Yoshimoto
Faculty of Agriculture, the University of Tokyo
Keywords: *Pseudomonas putida,* genetic transformation, plasmid

1988-212
シュードモナス属細菌 TMY1009 株による β-1 型モデル化合物の分解
羽生直人、小松徹史、鴨田重裕、鮫島正浩、善本知孝
東京大学農学部
Degradation of *β*–1 type lignin model compounds by *Pseudomonas* TMY1009
Naoto Habu, Tetsushi Komatsu, Shigehiro Kamota, Masahiro Samejima, Tomotaka Yoshimoto
Faculty of Agriculture, the University of Tokyo
Keywords: *erythro*-1,2-bis(4-hydroxy-3-methoxyphenyl)-1,3-propanediol, HPLC

1988-213
Fusarium solani M-13-1 による β−アリールエーテル結合の開裂と α−ケトンの還元生成物の絶対配置
片山健至、大浦健二、筒井丈二、十河村男
香川大学農学部
Cleavage of a β-aryl ether linkage by *Fusarium solani* M-13-1 and the absolute configuration of α-ketonic reduction products
Takeshi Katayama, Kenji Ohura, Jyoji Tsutsui, Murao Sogo
Faculty of Agriculture, Kagawa University
Keywords: glycerol-2-aryl ether, guaiacylglycerol-β-(vanillic acid) ether, UV spectroscopy, HPLC, ^{1}H-NMR

1988-214
カワラタケ菌体外酵素によるリグニン生分解機構の解析
飯村洋介[*1]、片山義博[*1*2]、田村利香[*1]、諸星紀幸[*1]、原口隆英[*1]
[*1] 東京農工大学農学部、[*2] 神戸製鋼生物学研究所
Analysis of the biodegradation mechanism of lignin by extracellular enzyme of *Coriolus vercicolor*
Yosuke Iimura[*1], Yoshihiro Katayama[*1*2], Rika Tamura[*1], Noriyuki Morohoshi, [*1] Takafusa Haraguchi[*1]
[*1]Faculty of Agriculture, Tokyo University of Agriculture and Technology, [*2]Biotechnology Research Laboratory Kobe Steel, Ltd.
Keywords: laccase Ⅲ, ^{13}C-DHP, ^{14}C-DHP, HPLC, ^{13}C-NMR

1988-215
木材腐朽菌によるリグニンモデル配糖体の生成について（V）
近藤隆一郎、今村博之
九州大学農学部
Formation of lignin model glycosides by wood-rotting fungi (V)
Ryuichiro Kondo, Hiroyuki Imamura
Faculty of Agriculture, Kyushu University

Keywords: *Betula platyphylla, Tyromyces palustris, Coriolus versicolor, Phanerochaete chrysosporium*, veratryl alcohol, veratraldehyde

1988-216
DHP 及びその配糖体の酵素分解
飯森武志[*1]、迫 孝[*1]、近藤隆一郎[*1]、今村博之[*1]、西田友昭[*2]
[*1] 九州大学農学部、[*2] 神戸製鋼生物学研究所
Enzymatic degradation of DHP and its glycoside
Takeshi Iimori[*1], Takashi Sako[*1], Ryuichiro Kondo[*1], Hiroyuki Imamura[*1], Tomoaki Nishida[*2]
[*1]Faculty of Agriculture, Kyushu University, [*2]Biotechnology Research Laboratory, Kobe Steel, Ltd.
Keywords: *Phanerochaete chrysosporium*, lignin peroxidase, laccase, horse radish peroxidase

1988-217
遊離のフェノール性水酸基を持つ DHP のリグニンペルオキシダーゼによる分解
梅澤俊明、樋口隆昌
京都大学木材研究所
Degradation of DHP with free phenolic hydroxyl group by lignin peroxidase
Toshiaki Umezawa, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: *Phanerochaete chrysosporium*, phenolic OH, GC-MS, β-*O*-4 bond cleavage

1988-218
微生物によるリグニン分解（第 4 報）—高活性、高選択性リグニン分解菌 IZU−154 株を前処理に用いた木材糖化プロセス—
西田友昭、中山雄之、三村精男、高原義昌
神戸製鋼所生物学研究所
Lignin biodegradation by wood rot fungi (IV) -Wood hydrolysis process using highly active and highly selective lignin degrading fungus IZU-154—
Tomoaki Nishida, Tsuyoshi Nakayama, Akio Mimura, Yoshimasa Takahara
Biotechnology Research Laboratory, Kobe Steel Ltd.
Keywords: *Fagus crenata, Coriolus versicolor,* wood saccharification, enzymatic hydrolysis, Klason lignin

1988-219
機械パルプの菌体外酵素による漂白
山下民治[*1]、橘 燦郎[*2]、大島喜八郎 [3]、住本昌之[*2]
[*1] 中越パルプ工業株式会社、[*2] 九州大学農学部、[*3] 十條製紙株式会社
Bleaching of mechanical pulp by extracellular enzyme
Tamiharu Yamashita[*1], Sanro Tachibana[*2], Kihachiro Ohshima[*3], Masashi Sumimoto[*2]
[*1]Chuetsu Pulp & Paper Co. Ltd, [*2]Faculty of Agriculture, Kyushu University, [*3]Jujo Paper Co. Ltd.
Keywords: *Phanerochaete chrysosporium*, *Coriolus versicolor,* brightness, post color number

第34回（1989.10.16-17）名古屋大学農学部

1989-101
圧縮試料のX線回折法などによるミクロフイブリル配向分布の計測とリグニンの堆積
畑　茂樹、藤田　稔、佐伯　浩
京都大学農学部
Measurement of distribution of microfibril orientation and lignin deposition in the compressed sample by X ray diffraction
Shigeki Hata, Minoru Fujita, Hiroshi Saiki
Faculty of Agriculture, Kyoto University
Keywords: *Cryptomeria japonica, Chamaecyparis obtusa,* UV microspectroscopy

1989-102
液体窒素下で破砕された細胞壁断片におけるリグニン分布と多様性の検討
吉永　新、藤田　稔、佐伯　浩
京都大学農学部
Distribution and diversity of lignin in cell wall pieces obtained by cryomilling in liquid nitrogen
Arata Yoshinaga, Minoru Fujita, Hiroshi Saiki
Faculty of Agriculture, Kyoto University
Keywords: *Chamaecyparis obtusa, Betula maximowicziana, Quercus crispula,* secondary wall, middle lamella, UV microspectroscopy, Mäule color reaction,

1989-103
イチョウにおけるリグニンの形成と構造
福島和彦、寺島典二
名古屋大学農学部
Formation and structure of lignin in ginkgo
Kazuhiko Fukushima, Noritsugu Terashima
Faculty of Agriculture, Nagoya University
Keywords: microautoradiography, radio tracer, nitrobenzene oxidation, xylem differentiation

1989-104
草本植物リグニン中の*p*–hydroxyphenyl 核
飯山賢治[*1]、Thi Bach Tuyet Lam[*2], Bruce A. Stone[*2]
[*1] 東京大学農学部、[*2]La Trobe 大学生化学科
p–Hydroxyphenyl nucleus in herbaceous plant lignin
Kenji Iiyama[*1], Thi Bach Tuyet Lam[*2], Bruce A. Stone[*2]
[*1]Faculty of Agriculture, the University of Tokyo, [*2]Department of Biochemistry, La Trobe University, Australia
Keywords: wheat, *Triticum aestivum*, nitrobenzene oxidation, cinnamic acid

1989-105
イネ科植物細胞壁中のLCC結合 —Ferulic acid bridge—
飯山賢治[*1]、Thi Bach Tuyet Lam[*2], Bruce A. Stone[*2]
[*1] 東京大学農学部、[*2]La Trobe 大学生化学科
LCC bonds in cell wall of Gramineous plant, –Ferulic acid bridge
Kenji Iiyama[*1], Thi Bach Tuyet Lam[*2], Bruce A. Stone[*2]
[*1]Faculty of Agriculture, the University of Tokyo, [*2]Department of Biochemistry, La Trobe University, Australia
Keywords: *Triticum aestivum*, wheat internode, ferulic acid, cinnamic acid, diferulic acid

1989-106
E1 リグニンの起源と性状
松本雄二、桃原郁夫、石津　敦
東京大学農学部
Origin and character of E1 lignin

Yuji Matsumoto, Ikuo Momohara, Atsushi Ishizu
Faculty of Agriculture, the University of Tokyo
Keywords: chlorine bleaching, E1 effluent, chlorinated lignin, alkaline treatment, GPC

1989-107
Cloning of bi-functional O-methyltransferase from aspen (*Populus tremuloides*)
Robert C. Bugos, Vincent L. Chiang, Wilbur H. Campbell
Michigan Technological University
Keywords: ion exchange chromatography, affinity chromatography,

1989-108
リグニン生合成制御に関する研究 アンチセンス法を用いたペルオキシダーゼの発現制御
刑部敬史[*1]、西田謙吾[*1]、山門幹子[*1]、片山義博[*2]、諸星紀幸[*1]
[*1] 東京農工大学農学部、[*2] 東京農工大学共同研究開発センター
Studies on the control of lignin biosynthesis, -Regulation of peroxidase expression by antisense RNA technology.-
Keishi Osakabe[*1], Kengo Nishida[*1], Mikiko Yamakado[*1], Yoshihiro Katayama[*2], Noriyuki Morohoshi[*1]
[*1]Faculty of Agriculture, Tokyo University of Agriculture and Technology, [*2] Cooperative Research Center, Tokyo University of Agriculture and Technology
Keywords: *Nicotiana tabacum*, antisense RNA, Ti plasmid

1989-109
リグニンモデル化合物分解酵素遺伝子のクローニング(XI) β–アリルエーテル結合開裂酵素遺伝子の解析
政井英司[*1]、片山義博[*2]、西川誠司[*1]、山崎眞狩[*3]、諸星紀幸[*1]
[*1] 東京農工大学農学部、[*2] 東京農工大学共同研究開発センター、[*3]東京大学農学部
Cloning of the gene for lignin model compounds degrading enzyme (XI), —Analysis of the gene encoding the enzyme of β–aryl ether cleavage
Eiji Masai[*1], Yoshihiro Katayama[*2], Seiji Nishikawa[*1], Makari Yamazaki[*3], Noriyuki Morohoshi[*1]
[*1]Faculty of Agriculture, Tokyo University of Agriculture, [*2]Cooperative Research Center, Tokyo University of Agriculture and Technology, [*3]Faculty of Agriculture, the University of Tokyo
Keywords: *Pseudomonas paucimobilis*, *Escherichia coli*, umbelliferone ether

1989-110
ビフェニル型リグニンモデル化合物芳香族炭素の化学シフトに及ぼす置換基の影響
青山政和[*1]、M. Drumond[*2], C. L. Chen[*2], D. Robert[*3]
[*1] 北海道立林産試験場、[*2] ノースカロライナ州立大学、[*3]C. E. N. G.
Effect of substituent groups on the chemical shift of aromatic carbons of biphenyl type lignin model compounds
Masakazu Aoyama[*1], M. Drumond[*2], * C.L. Chen[*2], D. Robert[*3]
[*1]Hokkaido Forest Products Research Institute, [*2]North Carolina State University, [*3]Centre d'Etudes Nucléaires de Grenoble
Keywords: ^{13}C NMR, *Picea glauca*, MWL,

1989-111
アルカリ性蒸解における針葉樹リグニンと広葉樹リグニンの反応性の差異（4）—イオン化示差スペクトルを用いたシリンギルリグニンの分布—
堤 祐司、近藤隆一郎、坂井克己、今村博之
九州大学農学部
Differences in the reactivity between lignins from softwood and hardwood during alkaline cooking (IV) —Distribution of syringyl lignin by ionization difference spectroscopy
Yuji Tsutsumi, Ryuichiro Kondo, Kokki Sakai, Hiroyuki Imamura
Faculty of Agriculture, Kyushu University
Keywords: *Pinus densiflora, Betula platyphylla,* dioxane lignin, syringyl lignin, guaiacyl lignin, GPC
1989-112
核交換法を用いたプロトリグニンの構造解析へのアプローチ

光永　徹、船岡正光、阿部　勲
三重大学生物資源学部
Approach to the structural analysis of proto lignin by the use of nuclear exchange method
Toru Mitsunaga, Masamitsu Funaoka, Isao Abe
Faculty of Bioresources, Mie University
Keywords: *Picea jezoensis, Betula maximowicziana, Phyllostachys* sp.*,* *Triticum* sp., nitrobenzene oxidation

1989-113
ESR による粉砕した含水リグノセルロース中のラジカル定量と粉砕挙動の解明
壁谷　洋
四国工業技術試験所
Quantitative determination of radicals in wet milled lignocellulose by ESR and investigation of behavior during milling
Hiroshi Kabeya
Government Industrial Research Institute, Shikoku
Keywords: TMP, cellulose powder, free radical, enzymatic hydrolysis,

1989-114
リグニンのメカノケミストリー（第 7 報）β−1 型リグニンモデル化合物のメカノケミカル反応
呉　宗華、松岡昌伸、李　典艶、住本昌之
九州大学農学部
Mechanochemistry of lignin (VII), -Mechanochemical reaction of β−1 type lignin model compounds
Zong-Hua Wu, Masanobu Matsuoka, Dian-Yan Lee, Masashi Sumimoto
Faculty of Agriculture, Kyushu University
Keywords: ceramic ball mill, vibratory ball mill, KRK type refiner, stilbene

1989-115
リグニンのラジカルスルホン化
渡辺正介、飯塚堯介、石津　敦
東京大学農学部
Radical-sulfonation of lignin
Shosuke Watanabe, Gyosuke Meshitsuka, Atsushi Ishizu
Faculty of Agriculture, the University of Tokyo
Keywords: sodium sulfite, oxygen, ethylguaiacol, GC-MS

1989-116
広葉樹硫酸リグニンの理化学的性質
安田征市、平野淳一
名古屋大学農学部
Physical and chemical properties of sulfuric acid lignins from hardwoods
Seiichi Yasuda, Junichi Hirano
Faculty of Agriculture, Nagoya University
Keywords: beech, *Fagus crenata*, MWL, Klason lignin, acid-soluble lignin, syringyl lignin, nitrobenzene oxidation, gel filtration, ^{1}H-NMR

1989-117
硫酸触媒による常圧酢酸パルプ化　—脱リグニン機構とリグニンの性質—
島本　周、佐野嘉拓
北海道大学農学部
Acetic acid pulping at atmospheric pressure with sulfuric acid as a catalyst, -Delignification mechanism and properties of lignin
Shu Shimamoto, Yoshihiro Sano
Faculty of Agriculture, Hokkaido University

Keywords: *Betula maximowicziana,* hydrogenolysis, GPC, ^{1}H-NMR, ^{13}C-NMR

1989-118
アルコール・バイサルファイト処理によるβ-*O*-4 結合の開裂反応について
高木孝夫、坂井克己、宮脇正一、今村博之
九州大学農学部
β-*O*-4 cleavage reactions during alcohol-bisulfite treatment
Takao Takagi, Kokki Sakai, Shoichi Miyawaki, Hiroyuki Imamura
Faculty of Agriculture, Kyushu University
Keywords: lignin model compounds, 2-propanol, isoeugenol, eugenol

1989-特別講演
葉肉単細胞培養系における木部細胞分化機構
福田裕穂
東北大学理学部
Invited lecture ; Differentiation mechanism of xylem cells in single mesophyll cells culture
Hiroo Fukuda
Faculty of Science, Tohoku University
Keywords: *Zinnia elegans*, tracheary element, secondary cell wall, lignin deposition, peroxidase

1989-201
リグニンの熱分解ガスクロマトグラフィー（第一報）分解生成物組成に及ぼす無機化合物の影響
黒田健一[*1]、井上嘉幸[*1]、坂井克己[*2]
[*1] 筑波大学農林工学系、[*2] 九州大学農学部
Pyrolysis gas chromatography of lignin (I), Effects of inorganic compounds on the composition of degradation products
Ken-ichi Kuroda[*1], Yoshiyuki Inoue[*1], Kokki Sakai[*2]
[*1]Institute of Agricultural and Forest Engineering, University of Tsukuba, [*2]Faculty of Agriculture, Kyushu University
Keywords: *Pinus densiflora, Chamaecyparis obtuse, Cryptomeria japonica,*

1989-202
膨潤-溶媒和のコンビネーションによる木材成分の迅速分離 —理論および分離挙動—
船岡正光、阿部 勲
三重大学生物資源学部
Rapid separation of wood constituents by the combination of swelling and solvation. -Theory and separation behavior
Masamitsu Funaoka, Isao Abe
Faculty of Bioresources, Mie University
Keywords: cresol, sulphric acid, temperature, wood refining

1989-203
膨潤-溶媒和法による木材成分の分離 —分離におよほす酸およびフェノール誘導体の効果—
船岡正光、深津俊輔、阿部 勲
三重大学生物資源学部
Separation of wood constituents by swelling –solvation method, —Effects of acid and phenol derivatives on separation—
Masamitsu Funaoka, Shunsuke Fukatsu, Isao Abe
Faculty of Bioresources, Mie University
Keywords: cresol, ethylphenol, propylphenol, guaiacol, chlorophenol, GPC

1989-204
リグニンにおけるジフェニルメタン型縮合構造の生成とその解裂
船岡正光、久保村実、阿部 勲

三重大学生物資源学部
Formation and cleavage of diphenylmethane type condensed structure in lignin
Masamitsu Funaoka, Minoru Kubomura, Isao Abe
Faculty of Bioresources, Mie University
Keywords: *Picea jezoensis, Betula maximowicziana,* nuclear exchange, nitrobenzene oxidation

1989-205
α−ケト β−アリールエーテル構造を有するモデル化合物の光分解
深川伸隆、石津　敦
東京大学農学部
Photolysis of α−keto, β-aryl ether type lignin model compounds
Nobutaka Fukagawa, Atsushi Ishizu
Faculty of Agriculture, the University of Tokyo
Keywords: β-aryl ether cleavage, coloration，high pressure mercury lamp,

1989-206
リグニンの水素化分解 —HRI の報告についての検討—
小山　実、金沢健治、小川博嗣
化学技術研究所
Hydrocracking of lignin, —Investigation of the report by HRI—
Makoto Koyama, Kenji Kanazawa, Hirotsugu Ogawa
National Chemical Laboratory for Industry
Keywords: HRI (Hydrocarbon Research Inc.) process, improved Noguchi process,

1989-207
シュードモナス属細菌 TMYl009 株のジアリールプロパン型モデル化合物の Cg 脱離酵素について
岸　克行[*1]、羽生直人[*1*2]、鮫島正浩[*1]、善本知孝[*1]
[*1] 東京大学農学部、[*2] ダイセル化学株式会社
Studies on the Cg eliminating enzyme from the diaylpropane type lignin model compounds produced by *Pseudomonas* sp. TMY1009
Katsuyuki Kishi[*1], Naoto Habu[*1*2], Masahiro Samejima[*1], Tomotaka Yoshimoto[*1]
[*1]Faculty of Agriculture, the University of Tokyo, [*2]Daicel Chemical Industries Ltd.
Keywords: gel electrophoresis, mass spectrometry

1989-208
リグノスチルベン-α、β-ジオキシゲナーゼ I に含有される鉄と酵素活性との関連性について
鴨田重裕[*1]、羽生直人[*1*2]、鮫島正浩[*1]、善本知孝[*1]
[*1] 東京大学農学部、[*2] ダイセル化学株式会社
Relationship between iron and enzyme activities in lignostylbene-α,β-dioxigenase I
Shigehiro Kamoda[*1], Naoto Habu[*1*2], Masahiro Samejima[*1], Tomotaka Yoshimoto[*1]
[*1]Faculty of Agriculture, the University of Tokyo, [*2]Daicel Chemical Industries Ltd.
Keywords: gel electrophoresis, Fe-chelater,

1989-209
バイオミメティック Mn／Co 触媒とリグニナーゼによる β-*O*-4 二量体の酸化分解反応
中川麻理子、島田幹夫、樋口隆昌
京都大学木材研究所
Oxidative degradation of β-*O*-4 type dimer by biomimetic Mn／Co catalyst and ligninase
Mariko Nakagawa, Mikio Shimada, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: *Phanerochaete chrysosporium*, lignin peroxidase, total ion chromatography

1989-210
白色腐朽菌による漂白排液の脱色：モデル化合物の分解・代謝機構の検討

桃原郁夫、松本雄二、石津　敦
東京大学農学部
Decoloration of bleach effluent by white rot fungi: Degradation of model compounds and investigation of metabolic mechanism
Ikuo Momohara, Yuji Matsumoto, Atsushi Ishizu
Faculty of Agriculture, the University of Tokyo
Keywords: naphthoquinone, anthraquinone, lignin peroxidase

1989-211
白色腐朽菌による漂白排水の突然変異原性の除去
渋谷征男、松本雄二、石津　敦
東京大学農学部
Removal of mutagenicity from bleach effluent by white rot fungi
Masao Shibuya, Yuji Matsumoto, Atsushi Ishizu
Faculty of Agriculture, the University of Tokyo
Keywords: *Phanerochaete chrysosporium*, 1,3-dichloroacetone, Ames test

1989-212
シリンギル及びビフェニール型リグニンモデル化合物芳香環のリグニンペルオキシダーゼによる開裂
服部武文、島田幹夫、樋口隆昌
京都大学木材研究所
Aromatic ring cleavage of syringyl and biphenyl type lignin model compounds by lignin peroxidase
Takefumi, Hattori, Mikio Shimada, Takayoshi Higuchi
Wood Research Institute, Kyoto University
Keywords: *Phanerochaete chrysosporium*, non-phenolic syringyl type compounds, ^{1}H-NMR, GC-MS,

1989-213
カワラタケによるリグニン生分解機構の解析
飯村洋介、片山義博、田村利香、中村雅哉、諸星紀幸
東京農工大学農学部
Investigation of lignin biodegradation mechanism by *Coriolus vercicolor*
Yosuke Iimura, Yoshihiro Katayama, Rika Tamura, Masaya Nakamura, Noriyuki Morohoshi
Faculty of Agriculture, Tokyo University of Agriculture and Technology
Keywords: ^{14}C tracer, ^{13}C tracer, ^{14}C -DHP, ^{13}C-DHP, GPC

1989-214
木材腐朽菌によるリグニンモデル配糖体の生成について(VII) カワラタケによるキシロース配糖体の生成機構
迫　孝、近藤隆一郎、今村博之
九州大学農学部
Formation of lignin model glycoside by wood rotting fungi (VII), Formation mechanism of xyloside by *Coriolus vercicolor*
Takashi Sako, Ryuichiro Kondo, Hiroyuki Imamura
Faculty of Agriculture, Kyushu University
Keywords: ^{14}C tracer, ^{14}C-glucose, ^{13}C tracer, ^{13}C-glucose, ^{13}C-NMR

1989-215
木材腐朽菌によるリグニンモデル配糖体の生成について(VIII) カワラタケによるリグニン生分解おけるキシロース配糖体生成の役割
迫　孝、山上　陽、近藤隆一郎、今村博之
九州大学農学部
Formation of lignin model glycoside by wood rotting fungi (VIII), The role of the formation of xyloside in biodegradation of lignin by *Coriolus vercicolor*
Takashi Sako, Hikari Yamagami, Ryuichiro Kondo, Hiroyuki Imamura

Faculty of Agriculture, Kyushu University
Keywords: *Fagus crenata* , ^{14}C tracer, ^{14}C-glucose, veratryl-β-D-xyloside, GPC

1989-216
リグニン・多糖複合体のモデル高分子 —細胞特異性の生医学材料としての応用— 小林一清[*1]、赤池敏宏[*2]
[*1] 名古屋大学農学部、[*2] 東京農工大学工学部
Macromolecular models of lignin-polysaccharide complex, —Application to cell-specific biomedical material
Kazukiyo Kobayashi[*1], Toshihiro Akaike[*2]
[*1]Faculty of Agriculture, Nagoya University, [*2]Faculty of Engineering, Tokyo University of Agriculture and Technology
Keywords: LCC, oligosaccharide-carrying polystyrene, oligosaccharide, hepatocytes

1989-217
水溶性リグニンの免疫活性及び抗ウイルス活性
鈴木春巳[*1]、飯山賢治[*1]、栃倉匡文[*2]、山崎素直[*1]、山本直樹[*2]、戸田昭三[*1]
[*1] 東京大学農学部、[*2] 山口大学医学部
Immunological and antiviral activities of water soluble lignin
Harumi Suzuki[*1], Kenji Iiyama[*1], Tadafumi Tochikura[*2], Sunao Yamazaki[*1], Naoki Yamamoto[*2], Shozo Toda[*1]
[*1]Faculty of Agriculture, the University of Tokyo, [*2]School of Medicine, Yamaguchi University
Keywords: *Lentinus edodes*, bagasse, lignosulfonate, polyanion

1989-218
リグニン樹脂接着剤の製造
佐野嘉拓、遠藤　稔、遠藤健一
北海道大学農学部
Production of lignin based adhesives
Yoshihiro Sano, Minoru Endo, Kenichi Endo
Faculty of Agriculture, Hokkaido University
Keywords: *Abies sachalinensis,* cresol lignin, kraft lignin, lignin-phenol resin

1989-219
光学活性基を有するリグニン関連型液晶の合成とその物性（1）
春日和行[*1]、畠山兵衛[*1]、畠山立子[*2]
[*1] 製品科学研究所、[*2] 繊維高分子材料研究所
Synthesis and properties of lignin-related liquid crystal with optically active groups (I)
Kazuyuki Kasuga[*1], Hyoe Hatakeyama[*1] Tatsuko Hatakeyama[*2]
[*1]Industrial Products Research Institute, [*2]Institute for Textiles and Polymers
Keywords: DSC, X-ray diffraction, vanillic acid methyl ester

1989-特別講演
リグニンはどのように糖と結合するか
越島哲夫
京都大学木材研究所
Invited lecture ; How lignin is bonded to carbohydrate ?
Tetsuo Koshijima,
Wood Research Institute, Kyoto University
Keywords: *Pinus densiflora,* Björkman LCC, GPC, DDQ, 2.3-dichloro-5.6-dicyano-*p*-benzoquinone,

第35回（1990.10.15-16）東京大学 山上会館

1990-101
水溶性リグニンの溶液中の挙動
渡辺正介、飯塚堯介、石津　敦
東京大学農学部
Behavior of water soluble lignin in aqueous solution
Masasuke Watanabet, Gyosuke Meshitstlka, Atsushi lshizu
Faculty of Agriculture. the University of Tokyo.

Abstract: Behavior of water soluble lignin in ion-exchanged water in the presence of surface-active agents, such as sodium dodecylsulfate (SDS) and sodium dodecylbenzenesulfonate(SDB), vas investigated with gel filtration chromatography using Sepharose CL-2B. With a surface-active agent, a remrkable change in gel filtration curves of sodium lignosulfonate (LSA). that is, shift to at low molecular weight region was observed. These results seen to indicate the aggregation of LSA molecules which carry both of hydrophilic and hydrophobic domains, and the molecular association of LSA was thought to be attributed to the hydrophobic inter molecular interaction.

1990-102
ポリフエノール類のタンパク質吸着能について
河本晴雄、中坪文明、村上浩二
京都大学農学部
Protein–adsorption capacily of polyphenols
Haruo Kawamoto, Fumiali Nakatsubo, Kouji Murakami
Protein–adsorption capacity of polyphenols

Abstract: Several kinds of condensed tannins were successfully synthesized and the relationships between the structure and the protein precipitating capacity were examined. This examination revealed that the distribution pattern of the phenolic hydroxyl groups in tannin molecule, not the existence of *o*-dihydroxyl- phenyl groups, is important for higher protein-precipitating capacity. Thus, these results suggest that 1ignin should also have the protein-adsorption capacity, if the phenolic hydroxyl groups are located in the appropriate positions of lignin molecule. Then, the protein-adsorption capacity of several kinds of lignins was tested. Consequently, thiolignin and steam explosion lignin were found to have the higher capacity than commercial available immobilized tannin.

1990-103
放射線照射によるリグニンの特性変化について
古屋信子、菱山正二郎、須藤賢一
森林総合研究所
Characterization of lignin from γ-ray irradiated wood
Nobuko Furuya, Shojiro Hishiyama, Ken-ichi Sudo
Forestry and Forest Products Reserch Institute

Abstract: The chemical feature of lignin from wood irradiated by 25-100 Mrad of γ-ray irradiated was investigated. The dioxane lignin (DL) was isolated from untreated and irradiated woods according to Pepper's method. The yield of DL was higher compared with that of untreated wood, though it depends on the radiation dose. The yielcl of DL from the wood treated by 50 Mrad of irradiation dose was about 40%, whereas that from the untreated wood was 27%. The average molecular weight of DL from the irradiated wood increased with increasing the irradiation dose. The amounts of phenolic-OH and methoxyl groups in DL decreased with increasing the irradiation dose. The relative amounts of C and H in DL from γ-irradiated wood had a tendency to decrease, whereas that. of oxygen increased. The yield of nitrobenzene oxidation products ranged from 11.9 to 18.2% depending to the irradiation dose. This shows that lignin in wood changes both decomposition and condensation by γ-irradiation. From these results, it is indicated that lignin in wood changes in the chemical structure to some extent in mo1ecular weight, functional groups and so on.

1990-104
リグニンの水素化分解 —数種の触媒の検討—
小山　実
化学技術研究所
Hydrocracking of lignin, —Montmorillonite catalysts—
Makoto Koyama

National Chemical Laboratory for Industry

Abstract: A kraft lignin (KL) and lignin model diners were hydrocracked with Fe-, Ni-. Co-, and Mo-montmorillonite-S (Mo-Mtm-S) as catalysts. Yields of monophenols and benzenes from hydrocracking of 2-hydroxybiphenyl by 450 ºC, 50 minutes with Fe-Mtm-S were about 10 and 25 %, respectively. About hydrocracking of KL with Fe-Mtm-S, yields of monophenols were similar to, but depolymerization of KL was more promoted than it with Fe/Alumina-S catalyst.

1990-105
リグノセルロース熱分解物を原料とするポリウレタンの熱的性質
広瀬重雄、畠山兵衛
製品科学研究所
Thermal properties of polyurethanes derived from thermal degradation products of lignocellulose Shigeo Hirose, Hyoe Hatakeyama
Industrial Products Research Institute, Tokyo

Abstract: A liquid and charcoal were obtained by the thermal degradation of Eucalyptus.
The liquid was distilled at 230 ºC and the solid residue was obtained. The residue was found to contain 5.8 mmol/g of the hydroxyl group. Polyurethanes (PU's) were prepared from the residue, polyethylene glycol (PEG) 400 and diphenylmethane diisocyanate (MDl). Thermal degradation of PU's Was studied by thermogravimetry (TG). The effect of the addition of residue to PU,s is considered in this paper.

1990-106
ユーカリリグニンからのポリウレタンフォームの力学的性質
中村邦雄[*1]、畠山兵衛[*2]、J. Meadows[*3]、P.A. Williams[*3]、G.0. Phillips[*3]
[*1] 大妻女子大学, 製品科学研究所、[*3]Northeast Wales Institute
Mechanical properties of polyurethane foam derived from *Eucalyptus* lignin
Kunio Nakamura[*1], Hyoe Hatakeyama[*2], J. Meadows[*3], P.A. Williams[*3]、G.0. Phillips[*3]
[*1]Otuma Women's University, [*2]Industrial Products Research Institute, [*3]Northeast Wales Institute

Abstract: Polyurethane (PU) from Eucalyplus lignin (EL) and polyol were prepared as follows: EL
was dissolved ln polyethylene glyco1 (PEG) having a molecular Weight of 400 at 50 ºC for1 hour. PU foam was obtained by the reaction between the polyol and diphenylmethane diisocyanate (MDl). The EL content in PU foam and MDl/polyol ratio were varied in order to obtain different kinds of PU foam. The density of PU foam, compression strength and elasticity were measured using the weight method and a LLoyd INSTRUME:NT T30K Mode1. Thermal properties of the PU foam prepared were measured by differential scannlng calorimetry (DSC).

1990-107
リグニン系炭素繊維の基礎物性とその応用
中嶋信之[*1]、横山　昭[*1]、須藤賢一[*2]、志水一允[*2]
[*1] 日本カーボン株式会社、[*2] 森林総合研究所
Propert.ies and applications of lignin based carbon fiber
Nobuyuki Nakajima[*1], Akira Yokoyama[*1], Kenichi Sudo[*2], Kazumasa Shimizu[*2]
[*1]Nippon Carbon Co., Ltd., [*2]Forestry and Forest Products Research Institute,

Abstract: Preparation methods for lignin based carbon fiber (LCF) were investigated. Raw lignin was extracted from steam-exploded white birch. After mild hydrocracking followed by heat treatment under reduced pressure, the lignin shoved excellent spinnability in melt-state. Crystallinity of LCF is somewhat lower than that of another kind of carbon fiber. As to mechanical properties, LCF is classified into general purpose carbon fiber. Tensile strength of LCF is 40-60kg/mm^2. After steam activation, the specific surface area increased to 2000m^2/g. The bending strength of LCF/cement composite was about 100kg/cm^2 at 7vol.% fiber content. LCF/Epoxy-resin composite showed the bending strength of 25-30kg/mm^2 and about 3kg/mm^2 of inter laminar strength.

1990-108
Albizia falcata 材のリグニン・多糖結合体について
渡辺隆司[*1]、今村剛士[*1]、越島哲夫[*2]、Myrtha Karina[*3]
[*1] 京都大学木材研究所、[*2] 近畿大学農学部、[*3]LIPI,P3FT

Lignin-carbohydrate complexes from *Albizia falcata* wood
Takashi Watanabe[*1], Takeshi lmamura[*1], Tetsuo Koshijima[*2], Myrtha Karina[*3]
[*1]Wood Research Institute, Kyoto University, [*2]Faculty of Agriculture Kinki University, [*3]Research and Development Centre for Applied Physics. Indonesian Institute of Sciences

Abstract: Lignin-carbohydrate complexes (LCCs) were isolated from tropical hard wood of *Albizia falcata* Backer by a modified Björkman method. After extraction of milled wood lignin from the hard wood, LCCs were isolated by successive extraction of the wood residue with water and 4% aqueous NaOH. NMR and rnethylation analysis indicated that the alkali-soluble fraction was composed of glucuronoxylan-lignin complex and that a neutral xylan chain existed in the water-soluble LCC fraction.

1990-109
Forsythia intermedia のリグナン生合成酵素について
梅澤俊明（Toshiaki Umezawa ）[*1]、Laurence B. Davin[*2]、Norman G. Lewis[*2]
[*1]Commonwealth Center for Wood Science and Technology/ [*2]Department of Biochemistry, Virginia Polytec Institute and State University
Formation of optically pure lignans by cell free extracts of *Forsythia Intermedia*
Toshiaki Umezawa, [*1], Laurence B. Davin[*2], Norman G. Lewis[*2]
[*1]Commonwealth Center for Wood Science and Technology/ [*2]Department of Biochemistry, Virginia Polytec Institute and State University

Abstract: A crude cell-free extract from *Forsythia IntermEdina* catalyzes the formation of (-) -secoisolaliciresinol, and not its (+) –enantiomer, when incubated with coniferyl alcohol in the presence of NAD(P)H and H202. This extract also catalyses the oxidation of (-)-secoisolariciresinol, but not its (+)-enantiomer, to (-)-matairesino1. This is the first report of an enzyme reaction specifically involved in the coupling between two phenyl-propanoid monomers to afford an optically pure lignan.

1990-110
リグノール類の脱水素重合
内田洋介、寺島典二
名古屋大学農学部
Dehydrog:enative polymerization of lignols
Yousuke Uchida, Noritsugu Terashima
Faculty of Agriculture, Nagoya University

Abstract: In order to examine the factors affecting formation of condensed structures in protolignin macromolecule, coniferyl alcohol, *p*-coumaryl alcohol and sinapyl alcohol were polymerized dehydrogenatively under different pHs and in the presence of different kinds of polysaccharides. The proportion of three main dilignols, β-0-4, β-5, and β-βtypes, formed in the earliest stage of polymerization was affected greatly by the pH. Under low pH and in the presence of an acidic polysaccharide, pectin, the proportion of condensed type β-5 dimer, dehydrodiconiferyl alcohol, was higher than that found under high pH and in the absence of pectin or in the presence of less acidic hemicelluloses.

1990-111
広葉樹培養細胞のリグニン生成とペルオキシターゼアイソザイムの基質特異性について
堤 裕司、坂井克己
九州大学農学部
Lignin biosynthesis and substrate specificities of peroxidase isoenzymes with respect to syringyl and guaiacyl structures in angiosperm tree callus cultures
Yuji Tsutsumi, Kokki Sakai
Faculty of Agriculture, Kyushu University

Abstract: We investigated the possibility that substrate specificities of peroxidase isoenzymes can control syringyl lignin contents in xylem tissues. Peroxidase isoenzymes from *Populus* callus cultures were fractionated to three isoenzyme groups, soluble peroxidase (SPO), ionically bound peroxidase (IPO) and wall bound peroxidase (WPO). The substrate specificities of these isoenzyme groups with respect to syringyl and guaiacyl substrates were investigated. The speclflcity of IPO to syringyl substrate was the highest, among three peroxidase isoenzyme groups. Though the severe water stress applied to the calluses elevated both their lignin content and peroxidase levels, the specificity to syringyl substrate and syringyl lignin content determined by nitrobenzene oxidation were decreased. The peroxidase isoenzyme groups from *Cryptomeria* calluses exhibited the lower specificity to a syringyl substrate. These results suggest that the syringyl lignin biosynthesis is controlled not only by the lignin monomer supply but also by the substrate specificity of peroxidase in the last step of lignin formation, that is dehydrogenetive polymerization catalyzed by peroxidase in angiosperm xylem tissues.

1990-112
食用担子菌の生産するフエノール酸化酵素
小藤田久義、太田朋子、松下敦史、麻田恭彦、桑原正章
香川大学農学部
Phenol oxidase and peroxidase produced by edible mushrooms
Hisayoshi Kofujita, Tomoko Ohta, Atsushi Matsushita, Yasuhiko Asada,
Masaaki Kuwahara
Faculty of Agriculture, Kagawa University,

Abstract: Phenol oxidase and peroxidases were produced by *Lentinus edodes* and *Pleurotus ostreatus* in liquid and solid state cultures containing low or high nitrogen source. Lignin peroxidase activity was negligible in these culture conditions. Laccase produced in the wheat bran medium by *L. edodes* and Mn(II)-peroxidase produced in the glucose-peptone medium by *P. ostreatus* were purified to homogeneity by various chromatography. In most properties of each enzyme, laccase of *L. edodes* and Mn(II)-peroxidase of *P. ostreatus* were similar to that of *Coriorus versicolor* or *Phanerochaete chrysosporium*. Both of these enzymes degraded the phenolic β-0-4 lignin substructure model compound, syringylglycerol-β-guaiacyl ether (I). The structure of degradation products indicated that these two enzymes catalyze alkyl-aryl cleavage of substrate I.

1990-113
木材腐朽菌による木材の水溶性化挙動について
迫　孝、近藤隆一郎、坂井克己
九州大学農学部
Water solubilization of wood by white-rot fungi during wood decaying process
Takashi Sako, Ryuichiro Kondo and Kokki Sakai
Faculty of Agriculttlre, Kyushu University

Abstract: In previous papers, we reported that *Coriolus versicolor* transformed lignin model compounds into their xylosides in various sugar media. We tried to clarify the possibility of the formation of lignin-glycosides during the biodegradation of lignin by *C. versicolor* in ^{14}C-glucose and ^{13}C-glucose media. On the basis of the results of the incorporation of radioactivities into fungus treated lignin and the ^{13}C-NMR spectrum of the treated lignin, it was suggested that lignin was possibly transformed into its xylosides by *C. versicolor*. To get a better understanding of biodegradation of wood by wood-rot fungi, we attempted to decay beech wood meal with by white-rot fungi, *C. versicolor* and *Phanerochaete chrysosporium* for various period, and investigated the water soluble fraction of decayed wood meals. In *C. verslcolor* cultivation, the lignin components in the water soluble fraction were seemed to be degraded severely. On the other hand, the dissolved lignin components from wood meals decayed by *P. chrysosporium* were seemed to be relatively stable in the culture medium. Therefore, it was suggested that these fungi might have different catabolic system to degrade lignin.

1990-114
ベラトリル β-D-キシロシド共存下におけるリグニンペルオキシターゼによるリグニンモデル化合物の分解
服部武文、島田幹夫、樋口隆昌
京都大学木材研究所
Degradation of a lignin model compound by lignin peroxidase in the presence of veratryl β–D-xyloside
Takefumi Hattori, Mikio Shimada, Takayoshi Higuchi
Wood Research Institute, Kyoto University

Abstract: Addition of veratryl alcohol and/or veratryl β-D-xyloside enhanced Cα-Cβ cleavage reaction of l,2-bis(4-methoxyphenyl)propane-l,3-diol (I) which was a poorer substrate for lignin peroxidase than veratryl alcohol. The rate of degradation (I) was greater with veratryl alcohol than with veratryl β-D-xyloside, however veratryl β-D-xyloside was more stable than veratryl alcohol during reaction. Mixed type of competitive and noncompetitive inhibition pattern of Lineweaver-Burk plots obtained suggests that veratryl alcohol not only prevent lignin peroxidase from inactivation but also acts as a radical mediator.

1990-115

キノン型化合物のリグニンパーオキシダーゼによる分解

桃原郁夫、松本雄二、石津　敦
東京大学農学部

Degradation of a quinone model compound by lignin peroxidase

Ikuo Momohara, Yuji Matsumoto, Atsushi Ishizu
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Keywords: *Phanerochaete chrysosporium*, 1ignin peroxidase, superoxide anion, quinone, decolorization, veratryl alcohol

Abstract: A quinone model compound, 2-hydroxy-1,4-naphthoquinone (HNQ), is degraded by lignin peroxidase when veratryl alochol is present. Spectral study of this reaction system indicated that the presence of HNQ inhibits the oxidation of veratryl alcohol by lignin peroxidase and, thus, the formation of veratraldehyde starts only after the degradation of HNQ. Degradation rate was remarkably increased by the increase in veratryl alcohol concentration. Degradation was partly and completely prevented by adding a OH• scavenger (mannitol) and a O2-scavenger (Mn^{2+}), respectively. These results suggest that active oxygen species formed in lignin peroxidase - H2O2 - veratryl alcohol system play an important role in HNQ degradation.

1990-116

フエノール性 β-O-4 型リグニンモデル二量体のリグニンペルオキシダーゼによる分解

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Degradation of phenolic β–O-4 lignin model dirners by lignin peroxidase

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Abstract: Degradation of three kinds of phenolic β-O-4 1ignin model dimers,1-(4-hydroxy-3-methoxy-pheny1)-2-(2-methoxyphenoxy)-1,3-propanediol (I), 1-(4-hydroxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)-1,3-propanediol (II) and 1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxy-phenoxy)-1,3-propanediol (III), by lignin peroxidase was investigated. Of these three substrates, substrate III was degraded to the following six compounds: guaiacol (IV) , syringaldehyde (V), syringic acid (VI), 2,6-dimethoxy-*p*-hydroquinone (VII), 2-(2-methoxy-phenoxy)-2-propenal (IX), and 1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)-2-propene-1-one (X). The results showed that substrate III was degraded via alkyl-aryl cleavage, Ca-Cb cleavage, and Ca oxidation by lignin peroxidase.

1990-117

リグニンペルオキシダーゼ(LiP)系による新しいシュウ酸分解反応とその生理的意義

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A new enzymatic decarboxylation of oxalic acid by lignin peroxidase (Lip) system and its physiological role

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Abstract: A new enzymatic decarboxylation of oxalic acid by lignin peroxidase (LiP) system) was discovered. Oxidation of veratryl alcohol by LiP vas potently inhibited by oxalic acid. The inhibition analysis clearly showed that the type of inhibition is noncompetitive. The apparent noncompetitive inhibition of LiP is explained as such that the veratryl alcohol cation radical intermediate formed by LiP is reduced back to veratryl alcohol by oxalic acid and consequently formation of veratraldehyde is blocked. The addition of oxalic acid into the ligninolytic culture of *Phanerochaete chrysosporium* also inhibited decomposition of synthetic lignin to CO2. The results indicate that oxalic acid as a secondary metabolite of white-rot fungi controls lignin deconposition on one side and veratryl alcohol acts as a mediator for decomposition of oxalic acid on the other.

1990-118

特別講演: リグニンの生化学：生合成と生分解

樋口隆昌
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Special lecture: Lignin biochemistry: Biosynthesis and biodegradation

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Abstract: Lignin biosynthesis via shikimate-cinnamate pathways in plants, and the biosynthetic differences of guaiacyl- and syringyl lignins between gymnosperms and angiosperms have been elucidated by tracer experiments using ^{14}C labeled precursors and the following enzyme reactions. The main cleavage mechanisms of propyl side chain and aromatic ring opening of lignin model compounds and synthetic lignin (DHP) by white-rot fungi and their enzymes, lignin peroxidase and laccase have been elucidated using ^{2}H, ^{13}C and ^{18}O-labeled lignin substructure dimmers with ^{18}O2 and H2^{18}O. Side chains and aromatic rings of these substrates were cleaved via aryl cation radical and phenoxy radical intermediates, in reaction mediated only by lignin peroxidase and laccase.

1990-201

リグニンのメカノケミストリー（第 7 報）ベラトリルグリセロール-β-シリンガアルデヒドエーテルのメカノケミカル反応

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Mechanochemistry of lignin (VII), Mechanochemical reaction of veratryl-β-syringaldehyde ether
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Abstract: Veratrylglycerol-β-syringaldehyde ether (M) was treated with CBM, VBM and KRK-refiner to find out the mechanochemical conversion products. Under the conditions treated, about 20% of the starting materials (M) were converted to give veratryl propan-1-on-3-ol 1, syringaldehyde 2, 2,6-dimethoxy-*p*-hydroquiqone 3, 2,6-dimethoxy-*p*-benzoquinone 4, vanillin 5 , veratrylalcohol 6. syringaldehydeglycol ether 7 and a condensation product 8. Formation of a chromophore 2.6-dimethoxy-*p*-benzoquinone 4, a leucochromophore 2,6-dmethoxy-*p*-hydro- quinone 3 , and para-carbonylphenols 2 and 5 should be deeply related to the color of unbleached pulp and color reversion of bleached mechanical pulp.

1990-202

高収率パルプ製造時のリグニンの挙動 (III) *p*-カルボニルフエノールを有する β-O-4 型モデル化合物の合成とそのメカノケミストリー

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Behaviours of lignin during production of high-yield pulp (III) - Synthesis and mechanochemical conversions of β-O-4 lignin model compound having a para-carbonyl phenol -
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Abstract: Trials for the improved method of synthesis of β-O-4 lignin model compounds (I) [3-methoxy-4-hydroxy-α-(2-nethoxyphenoxy)- β-hydroxypropiophenone] were made first.
The second one (II) [3,5-dinethoxy-4-hydroxy-α-(2-methoxyphenoxy)- β-hydroxypropio- phenone], however, had to be synthesized by the relatively different method. By the Mechanical treatments of the latter model compound (II) as a representative of a biphenyl model (III) and a biphenyl ether model (IV) with VBM and CBM, 2,6-dimethoxy-*p*-benzoquinone and others were obtained in reasonable yields.

1990-203

クラフト蒸解中難分解性リグニンの漂白過程における反応

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Reactions of pulping-resistant structure in lignin during bleaching
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Abstract: Reactions of veratrylglycerol-α-ethyl-β-guaiacyl ether (VEG) during bleaching were investigated. This lignin model compound represents the kraft pulping-resistant and oxygen bleaching-resistant structures in lignin. By chlorine treatment, about 3 moles of chlorine per mole of VEG were very quickly taken up for the unfavorable chlorination reaction. Only after this chlorination reaction was observed the extensive demethylation reaction which leads to favorable delignification reaction. α-Ethyl ether was never cleaved by chlorine treatment. Nitrogen dioxide and chlorine dioxide were not reactive to VEG. Acetic acid containing small amount of HCl (0.1% w/v) effectively cleaved the α-ether bond giving almost theoretical yield of ethyl acetate. Acetic acid treatment of KP and oxygen bleached KP (KOP) resulted in large drop in kappa number (Fig. 2). As a conclusion, we propose new non-chlorine bleaching sequence: either Oxygen-Acid Treatment-Chlorine Dioxide or Acid Treatment-Oxygen-Chlorine Dioxide.

1990-204

さらしパルプ中に検出されるダイオキシンの前駆体に関する一考察　塩素経換反応におよぼすリグニンの影響

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An investigation on precursors of dioxins detected in bleached kraft pulp (Influence of lignin on chlorine substitution reaction in chlorine water)

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Abstract: The investigation was done to obtain a better understanding of the reason why the ratio of 2,3,7,8-tetrachlorodibenzofuran (TCDF) to 1,2,7,8-TCDP detected in bleached kraft pulp is almost two and of the precursors of PCDFs. The ratios of 2,3,7,8-TCDF to 1,2,7,8-TCDF formed during the chlorination of uncblrinated dibenzofuran without pulp in chlorine water at different reaction conditions are about one, respectively. And also the ratio with bleached pulp is one. But 2,3,7,8- TCDF was formed more than three tines of 1,2,7,8-TCDF during the chlorination of dibenzofuran with unbleached pulp using chlorine water. These results show that lignin of unbleached pulp oriented chlorine substitution in the chlorination using chlorine water and that unchlorinated dibenzofuran may be a precursor of PCDFs.

1990-205

N0$_2$前処理酸素漂白法の機構について

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Mechanism of nitrogen dioxide pretreatment for oxygen bleaching

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Abstract: Pretreatment of kraft pulp with nitrogen dioxde has been shown to be an effective method for both improvement of delignification and protection of carbohydrate degradation in oxygen bleaching. However, the mechanism of its action is not clear. The objective of this research is to learn more about the mechanism.

1990-206

硫酸触媒による広葉樹材の常圧酢酸パルプ化　—パルプ化条件の検討

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北海道大学農学部

Abstract: Aqueous acetic acid pulping of hardwoods at atmospheric pressure with a sulfuric acid catalyst pulping conditions

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Abstract: Pulping of hardwoods at atmospheric pressure with 90% AcOH containing a small amount of sulfuric acid was investigated. The hardwoods were boiled for 0.5 hours in 90% AcOH for pretreatment, and then for 2-3 hours in 90% AcOH with 1.6-2.0% H2SO4 of wood for pulping. The hardwoods used were classified roughly into three groups on basis of the results of pulping. The 1st, class (birch) is pulped with ease by these procedure, the 2nd class (alder, beech, eucalyputus and poplar) with less difficulty and the 3rd class (acacia) with difficulties. Also lignin model compounds with β−ether were degraded under similar conditions to the pulping of hardwoods in order to clarify the reaction mechanism of lignin. The β−ether compounds were found to be reacted by the same mechanism as acetic acid pulping without H2SO4 at elevated temperatures.

1990-207

硫酸触媒による広葉樹材の常圧パルプ化 —酢酸リグニンの樹脂接着剤への応用

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Pulping of hardwood at atmospheric pressure with sulfuric acid catalyst, –Preparation of lignin based resin adhesives

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Abstract: Utilization of lignin in the substrate of phenol resins was investigated. Commercial kraft lignin and acetic acid lignin (AWL) prepared by acetic acid pulping of birch at atmospheric pressure were used as lignin. A mixture of lignin and phenol was condensed with HCHO in aqueous methanol under alkaline conditions in order to produce phenol-type resins. When 80% of phenol was replaced by each lignin, the resulting resins met JIS for phenol-type resins. When 20% resorcinol added to the resins, the press temperature was depressed to 100ºC. AWL and lignin model compounds were reacted with HCHO under acidic conditions in order to yield more activated hydroxymethylated lignin. Lignin reacted under acidic conditions were found to contain twice amounts of hydroxymethyl groups than that under alkali conditions.

1990-208

オイルパーム副産物のケミサーモメカニカルパルプ化

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Chemi-thermomechanical pulp of oil palm byproducts

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Abstract: With increasing demand of pulp and paper production, the new raw materials for pulp have been investigated with the purpose of higher utilizing of ligno-cellulosic oil palm by-products. Empty fruit bunch frond and trunk were pulped by anthraquinone-KP and TMP process. From the yield and sheet properties, frond was selected as the optimum raw material and CTMP process the appropriate one. The fungus attack to frond was prevented by pretreatment with some chemicals, including alkalis, bunch ash. Plant scale CTM-pulping showed almost the same results as the laboratory studies using the alkali pretreated fronds. The rolled paper produced corrugating medium and corrugated boards with the satisfied strengths. The characteristics of CTMP waste water were also studied and the biological treatability was tested.

1990-209

未利用林産資源の酵素、微生物による変換利用（2）高知県産広華樹35種の水蒸煮処理パルプの酵素糖化率

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Enzymatic and microbial conversion of unused forest product resources for further utilization (II), The susceptibility to the enzymatic saccharification of steam-cooked pulps made from thirty-five hardwoods of Kochi growth

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Abstract: The Asplund pulps made from thirty-five Japanese hardwoods of Kochi growth were tested for their susceptibilities to the enzymatic saccharification with *Trichoderna viride* cellulase, "Meicelase P-1". After the chemical analyses of both wood meals of the sample woods and the pulps were made, the morphological features such as the fiber cell wall area and the fiber cell wall thickness of each wood samples were measured using art image analysis system. The overall correlations between the susceptibilities and the chemical and the morphological features showed that only the lignin contents of both wood meals and pulps have the strongest correlations. Detailed analyses are now being undertaken.

1990-210

微生物（IZU−154株）によるクラフトパルプの漂白（第2報）

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Biobleaching of kraft pulp by the fungus, IZU-154 (II)

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Abstract: The fungus, IZU-154 exhibited the high activity of brightening the beech kraft pulp. The pulp brightness increased by 21 points to 49% by a five-day treatment associated with a corresponding decrease in Kappa number from 20.9 to 9.3. Combined fungal (F) and chemical (CED) bleaching gave a pulp with the almost same brightness (88%) and bleaching yield (94%) as a conventionally CEDED bleached pulp. The FCED bleaching process could significantly reduce the use of chlorine-based chemicals and the pollution load of waste liquors, compared to the conventional CEDED process. This is also the first report that softwood kraft pulp was brightened by the fungal treatment; i.e. IZU-154 treatment increased the brightness of Japanese red pine (*Pinus densiflora*) kraft pulp by 3l point to 55.9% and decreased kappa number from 35.4 to 5.3.

1990-211

ジリグノール分解性好アルカリ性細菌のプロトプラスト融合及び融合株の性質

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Protoplast fusion of dilignol degradable alkalophilic bacteria and properties of the fusants

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Abstract: In order to improve lignin degrading ability of alkalophilic bacteria, intergeneric protoplast fusion was carried out. The procedure for protoplast fusion from two strains, *Corynebacterium* CM-432 and *Acinetobacter lwoffi* CM-401 has been established. As the selective pressure of the fusants, antibiotics, kanamycin and penicillin were used. Some promising fusants were isolated. The lignin model compounds degrading ability and APPL generating ability of the fusants were superior to those of the parental strains. However, the fusants have grown only on the medium of pH 8.5 and have been devoid of the adaptability for wide pH range such as parental strains.

1990-212

担子菌 *Phanerochaete chrysosporium* 及び *Bjerkandera adusta* の生産するリグニンパーオキシダーゼとその遺伝子

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Characterization of lignin peroxidases and its genes from basidiomycetes *Phanerochaete chrysosporium* and *Bjerkandera adusta*

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Abstract: The basidiomycetes *Phanerochaete chrysosporium* and *Bjerkandera adusta* produce multiple extracellular glycosylated heme peroxidases called ligninases or lignin peroxidases. We have purified and characterized major lignin peroxidases of their enzymes. The lignin peroxidase of *B. adusta* exhibited close similarity to lignin peroxidase of *P. chrysosporium* with respect to their basic properties. Also, lignin peroxidase genes have been cloned from a *P. chrysosporium* DNA library and a *B. adusta* DNA library. Nucleotide sequencing of the gene of *B. adusta* has revealed that the lignin peroxidase structural gene contains 1,116 bp of protein-encoding sequence of which 69 bp encode the signal peptide. Amino acid sequence homology between the coding gene of *B. adusta* and the lignin peroxidase gene of *P. chrysosporium* is 61%.

1990-213

合成 DNA プローブを用いたハイブリダイゼーションによるリグノスチルベン-α,β-ジオキシケナーゼ産生遺伝子の検出

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Detection of the gene encoding lignostilbeneα,βdioxygenases by hybridization with synthetic oligonucleotide probes

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Abstract: Lignostilbene a, b dioxygenases (LSDs) are the key enzyme responsible for the cleavage of the Cα-Cβdouble bonds in the metabolism of lignin related compounds by *Pseudomonas* sp. TMY1009 (Fig.1). To elucidate the catalytic mechanism of LSD, detailed knowledge of the enzyme structure is required. The analysis of the gene is enable to determine the primary structure of the enzyme. In this study, to clone the gene encoding LSDs, genomic library of *Pseudomonas* sp. TMY1009 was constructed with a cosmid vector and two oligonucleotides corresponding to the partial amino acid sequences of LSD-I were synthesized. Hybridization between the library and two probes was conducted and several positive colonies were detected (Table 1). The recombinant cosmid (pMSH25) from one of the positive colonies were digested with several appropriate restriction enzymes and the physical map of this cosmid was determined. Furthermore, the location of LSD gene was analyzed by Southern hybridization (Fig.2 and 3).

1990-214

リグニンモデル化合物分解酵素遺伝子のクローニング(XV)10.5 kbp EcoRI 断片の構造および機能の解析

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Cloning of the genes involved in degradation of lignin model compounds (XV),

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Abstract: We already reported the isolation of the 10.5 kbp *Eco*RI DNA restriction fragment from *P. paucimobilis* SYE-6 chromosomal DNA. When this DNA fragment was inserted in the *Eco*RI site of vector plasmid pKT 230, this recombinant plasmid (pVAO1) could transform the vanillic acid- negative strain *P. putida* PpY1100 to vanillic acid-positive phenotype. One of the genes carried on this fragment was protocatechuate 4,5-dioxygenase gene and recerltly complete nucleotide sequence of this was determined [1]. In this study, we showed that the location of protocatechuate 4,5-dioxygenase, 4-carboxy-2-hydroxymuconate-6-semialdehyde dehydrogenase and 2-pyrone- 4,6-dicarboxylic acid hydrolase genes on the10.5 kbp *Eco*RI fragment isolated from *Pseudomonas paucimobilis* SYK-6 chromosormal DNA.

[1] Noda,Y. and Nishikawa, S. et a1. *J. 8acteriol.*, 1990, Vo1.172,No.5, 2704-2709.

1990-215

リグニンモデル化合物分解酵素遺伝子のクローニング（XVI）β-エーテラーゼ（β-アリールエーテル開裂酵素）遺伝子の解析

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Molecular cloning and analysis of β-etherase gene of *Pseudomonas paucimobilis* SYK-6

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Abstract: β-Aryl ether cleavage is essential to the biological degradation of lignin. In this study, we succeeded in the first isolation of β-etherase gene from cosmid genonic library of *Pseudomorms paucimobilis* SYK-6. 1.9kbp *Sal* 1 fragment encoding β-etherase was subcloned into pUC19 and pTTQ19. This gene was expressed in *E. coli* and expressed products were analyzed. Analysis of nucleotide sequence of this gene is carrying out.

1990-216

フエニルアラニンアンモニアリアーゼとその遺伝子

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Phenylalanine ammonia-lyases and their genes

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Abstract: PAL and the genes were preliminary examined before studying PAL genes from woody plants. First, GenBank and EMBL databases were surveyed by using IDKAS for the primer design in relation to PCR amplification of the genes. Some of the primers were successfully applied to the Hindlll digested DNA fragment from IPBPAL(sweet potato). The PCR products cover ca. 200bp fragments localized on the high homologous region. Further studies are now on progress. Secondary, visualizing PAL activities, especially on the PAGE gel, was intended by using fluorescent TLC plate. The product was not visualized on the gel, to which crude enzyme extract was charged, but the method worked before the PAGE. The threshold concentration for the detection was less than 0.2 mM, which is equivalent to <0.2 nmole/ml. Detecting the product on the gel may need more sensitive another method.

1990-217

PCR を用いたフェニルアラニンアンモニアリアーゼ遺伝子の解析

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Phenylafanine ammonia-lyase genes isolated by PCR method

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Abstract: Polymerase chain reaction (PCR) is an *in vitro* method for the primer-directed enzymatic amplification of specific DNA sequences. We have used this technique to isolate phenyalanine ammonia-lyase (PAL) genes. The primers corresponding to highly conserved regions of the PAL genes were used and amplified partial genomic clones from poplar and tobacco plants. The nucleotide sequences of PCR products showing ~ 78.9% similarity with those of PAL genes for bean and parsley, and 89% similarity at the deduced amino acid level.

1990-218

アンチセンス RNA 法によるペルオキシダーゼの発現抑制

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Antisense RNA inhibion of peroxidase gene expression in trans genic tobacco

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Abstract: In order to inhibit of lignin forming peroxidase activities, we have attempted to introduce of antisense peroxidase gene into *N. tabacum*. Peroxidase isoenzymes were extracted from transformants and separated by isoelectric focusing. From the results of isoelectric focusing, dramatic changes were not observed between isoenyme patterns of wild type and those of transformants. And we obtained 9 clones containing parts of tobacco peroxidase genes (TPOX genes) by polymerase chain reaction method. Parts of TPOX genes were determined.

1990-219

Agrobacterium tumefaciens による樹木形質転換系の確立

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Constraction of transformation system of woody plant using *Agrobacterium tumefaciens*

Shinya Kajita[*1], Shinya Kawai[*1], Yoshihiro Katayama[*2], Noriyuki Morohoshi[*1], Hiroetu Wabiko[*3], Hiroshi Sano[*3], Kunio Hata[*4]
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Abstract: Poplar leaf disks were inoculated with *Agrobacterium tumefaciens* LBA 4404 carrying a disarmd Ti plasmid vector pB1121. T-DNA of this plasmid encodes two genes, one is neomycin phosphotransferase ll gene and the other is β-glucuronidase gene. The leaf disks were then transferred to selective medium containing kanamycin. Transformed callus were obtained within 10 days, band maintained by fortnighty subculture. These transformants stained with X-Gluc., while untransformed callus contrastively didn't. This transformation system will contribute to the genetic engineering of woody plants.

第36回（1991.10.14-15）北海道大学 学術交流会館

1991-101

急速凍結置換固定法による細胞壁木化過程の観察

猪股書恵、高部圭司、佐伯 浩

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Observations on lignification process of cell wall by rapid-freeze and substitution method

Fumie Inomata, Keiji Takabe, Hiroshi Saiki

Faculty of Agriculture, Kyoto University

Abstract: Lignification process of cell wall in conifer tracheid was observed by rapid-freeze and substitution method. The ultrastructural images indicate that the wall materials of newly deposition form an amorphous thin layer lining the cell wall. This layer consists of polysaccarides and much water. Subsequently cellulose microfibrils and hemicelluloses may be assembled to form hydrophilic ordered structure. Lignified region of the wall hardly suffers the ice crystal damage, showing that lignification cause the removal of water from unlignified cell wall. In the later stage of secondary wall lignification, egg-shaped rough- and/or smooth endoplasmic reticula appear in cytosol. They may participate in biosynthesis and/or transport of lignin precursor.

1991-102

広葉樹の生育地・管孔配列・細胞壁厚とリグニン成分

呉 晋、深沢和三、大谷 諒

北海道大学農学部

Lignin compoition in hardwoods in relation to habitat, porosity and cell wall thickness in wood

Jing Wu, Kazumi Fukazawa, Jun Ohtani

Faculty of Agriculture, Hokkaido University

Abstract: Guaiacyl (G) and syringyl (S) lignins were detected by VIS microspectrophotometry using Mäule color reaction test. 110 hardwood species in 94 genera and 51 families from 3 habitats of Ynnnan, China, have been investigated. The monomer composition of lignin in a particular area of wood tissue was influenced by the kind of cell elelents, vessel arrangement of woods, tree habitat and cell wall thickness. GS ratio among certain cells or tree could not be fixed by this method, but a rough estimation of it was made by the analysis from the spectrum. The variations may suggest the evolutionary stages of tree phylogeny.

1991-103

カエデ属におけるリグニン分布の多様性

平井陽子、深沢和三、呉 晋

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Distribnion of lignins on the genus *Acer*

Yoko Hirai, Kazumi Fukazawa, Jing Wu

Faculty of Agriculture, Hokkaido University

Abstract: Distribution of lignins on the genus *Acer* was investigated by Mäule reaction, Klason method and nitrobenzene oxidation. The Klason lignin content ranges from 20 to 25%, but some species have very high lignin contents (28-30%). The syringaldehyde-vanillin ratio (S/V) ranges from 0.3 to 3.0. The species which has higher lignin content has lower S/V values. All species were classified into 7 types by these results and absorption spectra of Mäule reaction.

1991-104

タケ、ササ細胞壁中のいくつかの成分について

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Some phenolic components of the cell walls of bamboos (*Phyllostachys edulis* and *Phyllostachys bambusoides* Sieb. et Zucc.) and banboo grass (*Sasa kurilensis* Makino et Shibata)

Sanro Tachibana[*1], Katsumi Ohkubo[*1], G.H.N. Towers[*2]

[*1]Faculty of Agriculture, Ehine University, [*2]Departnent of Botany, The University of British Columbia, Canada

Abstract: 4,4'-Dihydroxytruxillic acid (DTA), a photodimer of *p*-coumaric acid, and 4,4'-dihydroxy-3,3'-dimethoxytruxillic acid (FAD), a photodimer of ferulic acid, were identified as components of the cell walls of stems and leaves of the bamboo (*Phyllostachys edulis*) and the bamboo grass (*Sasa kurilensis* Makino et

Shibata). Caffei acid, sinapic acid, 5-hydroxyferulic acid as well as *p*-coumaric acid and ferulic acid were also identified. The amounts were determined by peak areas using GC/MS with stearyl alcohol as an internal standard. Existence of the two feruloyl esters, O-(5-feruloyl-α-L-arabinofuranosyl)-(1→3)-O-β-D-xylopyranosyl-(1→4)-D-xylopyranose and 5-O-feruloyl-α-L- arabinofuranose, in the hydrolysis products of the bamboo (*Phyllostachys bambusoides* Sieb. et Zucc.) cell walls was confirmed on TLC plate through comparison of the Rf values with that of authentic samples.

1991-105

ヘミセルロース中におけるシナピルアルコールの脱水素重合

吉田晋一、棚橋光彦、篠田善彦

岐阜大学農学部

Dehydrogenative polymerization of sinapyl alcohol in hemicelluloses solutions

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Faculty of Agriculture, Gifu University

Abstract: In a plant cell wall, lignin was deposited in the matrix of polysaccharides through the lignification process. To demonstrate the effect of hemicelluloses on dehydrogenative polymerization, sinapyl alcohol was dehydrogenated with horseradish peroxidase/H2O2 in the presence of pectin by Zulaufverfahren. Main reaction products, which were syringylglycerol-β- sinapyl alcohol ether, syringaresinol and unknown compound, were isolated after the acetylation by PTLC and analyzed by NMR and MS spectrometry. As a results, unknown compound identified 1,5-di(3,5-dimethoxy-4-hydroxyphenyl)-4-hydroxymethyl-5-hydroxy-1-pentene □β-γtype). This substructure would be presented in native lignin, and generated by ionic reaction through the extended quinone-methide-intermediate.

1991-106

リグニン—グルクロン酸間エステル結合の酸化的開裂とその定量分析への応用

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Oxidative cleavage of ester linkages between lignin and glucuronic acid and its application to their quantitative analysis

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Abstract: Conjugated acid between 2,3-dichloro-5,6-dicyano-1,4-benzoquirnone (DDQ) and protonic acid, which is more electrophilic than DDQ, was subjected to the oxidative cleavage of ester bonds between alkylaromatic compounds and glucuronic acid. When DDQ-TFA conjugate was allowed to react with benzylglucuronate, the ester bonds were quantitatively cleaved, while ethyl glucuronate was inert to the reaction due to its high oxidation potential. Application of the selective oxidation to the determination of lignin-glucuronic acid bonds in 1ignin-carbohydrate complexes (LCCs) is reported.

1991-107

イネのリグニンの ^{13}C による選択的標識

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Selective ^{13}C enrichment of rice stalk lignin

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Faculty of Agriculture, Nagoya University

Abstract: Carbon-13 enrichment of a specific carbon of rice stalk lignin was carried out by administration of coniferin-[α-^{13}C] and 4-O-β-D-glucoferulic acid-[α-^{13}C] to a growing rice plant. The ^{13}C content of a side chain α-carbon of rice stalk lignin reached about 10 times of the natural abundance. ln the ^{13}C-NMR spectra of cellulolytic enzyme lignin and acetal lignin showed intense signals corresponding to α-carbons. The enhanced signals provide useful information about structure of lignin and the linkages between lignin and carbohydrates in rice plant.

1991-108

ラジオトレーサー法によるリグニン試料中の残留炭水化物量の測定

今井貴規、寺島典二
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Quantitative determination of the residual carbohydrate in lignin-preparations by radiotracer technique
Takanori Imai, Noritsugu Terashima
Faculty of Agriculture, Nagoya University

Abstract: When myo-inositol-[2-^{3}H] was administered to a magnolia shoot, radioactivity was mainly incorporated into xylose obtained by sulfuric acid hydrolysis of newly formed xylem, whereas, no radioactivity was incorporated into vanillin and syringaldehyde obtained by nitrobenzene oxidation. This result indicates that xylan was labeled selectively in the tissue, To estimate the amount of residual carbohydrate remaining in Klason lignin, the xylan-labeled wood tissue was treated with sulfuric acid, and the radioactivity of the insoluble solid lignin was determined. The amount of residual carbohydrate originating from xylan in Klason lignin was estimated to be about 8 %.

1991-109

ミクロオートラジオグラフ法による樹幹先端部の木部分化とリグニン不均一形成に関する研究

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Heterogeneous lignification during the apical growth of magnolia shoot studied by microautoradiography
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Abstract: Heterogeneous formation of lignin in the primary xylem of magnolia was visualized by microautoradiography and UV microscopy. Protoxylem in the vascular bundle consists of some vessels with lignified spiral secondary wall and undifferentiated parenchyma whose lignification is much delayed than other kind of cells. The cells around the primary xylem were differentiated to be thick wall cells and lignified after the formation of secondary xylem. UV spectra showed that the vessel wall lignin of primary xylem was similar to that of secondary xylem and that pith lignin was similar to fiber secondary wall 1ignin which is syringyl-rich. It is proposed that lignification in the elongating shoot would proceed in accordance with cell differentiation under definite controlled manner.

1991-110

リグニン化学構造の不均一性

深川伸隆、飯塚堯介、西山正樹、石津　敦
東京大学農学部
Structural inhomogeneity of lignin
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Abstract: Structural inhomogeneity of lignin was clearly demonstrated by the isolation of two distinctive lignin fractions from birchwood periodate lignin. The first one is a predominatingly syringyl-rich, mostly β-O-4 linked lignin fraction, which has a molecular weight of not lower than a milled wood lignin. The second one is a low molecular weight fraction of guaiacyl-rich and highly condensed structure.

1991-111

核交換および過ヨウ素酸酸化の併用によるリグニン芳香核構造の解析

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[*1] 三重大学生物資源学部、[*2]NewYork 州立大、ESPRI
Structural analysis of lignin by a combined nucleus exchange - periodate oxidation method
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Abstract: The phenolic hydroxyl group is one of the most important functionalities significantly affecting the reactivity of lignin during various modification processes. The free phenolic hydroxyl content of lignin has been estimated by several methods such as UV and NMR spectroscopies, potentiometric titration or periodate oxidation. However, these conventional processes give only the data on its total amount. The combined nucleus exchange-periodate oxidation method provides the quantitative information on the distribution of phenolic hydroxyl group in guaiacyl and syringyl, condensed and non-condensed, and diphenylmethane type units which are important as secondarily formed condensed structures. In the present paper, the theory, the procedure, and its application to softwood and hardwood protolignins, isolated lignins and pulp residual lignins are discussed.

1991-112
TMSiI 処理によるリグニン中めエーテル結合の選択的開裂 —低分子生成物の性状
藤野謙一、飯塚堯介、石津　敦
東京大学農学部
Selective cleavage of ether bonds in lignin by trimethylsilyl iodide, - The character of the low molecular weight products -
Kenichi Fujino, Gyosuke Meshitsuka, Atsushi lshizu
Faculty of Agriculture, the University of Tokyo

Abstract: Trimethylsilyl iodide cleaves ether bonds in lignin selectively under very mild reaction conditions. Applying this agent to gaiacylglycerol-β-guaiacyl ether as a model compoud, it has been proposed that the cleavage reaction results from the iodination of the benzyl carbon followed by the formation of a α-β double bond and the cleavage of the β-aryl ether bond. In this paper we applied this agent to a periodate lignin. Some acetate derivatives of the degradatiton products were separated by TLC and analyzed by means of GC-MS.

1991-113
1,2-ジアリール-1,3-プロパンジオールの塩酸中の挙動
岩瀬幸彦、安田征市
名古屋大学農学部
Behavior of 1, 2-diaryl-1, 3-propanediol in hydrochloric acid
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Faculty of Agriculture, Nagoya University

Abstract: 1,2-Diguaiacyl-1,3-propanediol [α-^{13}C] , one of lignin structural models, was synthesized and then treated in refluxing 0.2N hydrochloric acid. The ^{13}C NMR analysis of the products strongly supported the already proposed reaction mechanism of so-called "acidolysis" and. at the same tine, confirmed no rearrangement of a methyl group in contrast with easy rearrangement of a hydrogen atom and a phenyl nucleus. Treatment of models in refluxing 5% hydrochloric acid afforded less low-molecular- weight compounds and more condensation products in comparison with acidolysis. Treatment of the models in concentrated hydrochloric acid recovered the starting compounds together with condensation products and tentative chlorides. These results accord the fact that hydrochloric acid lignin contains less condensed structural unit than sulfuric acid lignin.

1991-114
ウド（*Alaria cordata*）シンナミルアルコールデヒドロゲナーゼの精製
日尾野隆^{*1}、柴田大輔^{*1}、梅沢俊明^{*2}、樋口隆昌^{*3}
^{*1} 三井植物バイオ研究所、^{*2} 京都大学木質科学研究所、^{*3} 日本大学農獣医学部
Isolation and characterization of cinnamyl alcohol dehydorogenase from *Alaria cordata*
Takashi Hibino^{*1}, Daisuke Shibata^{*1}, Toshiaki Umezawa^{*2}, Takayoshi Higuchi^{*3}
^{*1}Mitsui Plant Biotechnology Research Institute, ^{*2}Wood Research Institute, Kyoto University,
^{*3}College of Agriculture and Veterinary Medicine, Nihon University

Abstract: A cinnamyl alcohel dehydrogenase (CAD) from *Alaria cordata* was purified about_ 2100 fold to homogeneity. The molecular weight of the enzyme was estimated by Superose 12 column to be 72,000. The enzyme preferred cinnamaldehydes and cinnamyl alcohol as substrates. The purified protein was subjected to BrCN cleavage and the resulting peptides were separated using reverse- phase HPLC for amino acid sequencing.

1991-115
エレクトロポレーション法によるアンチセンス PAL 遺伝子のタバコへの導入
日尾野隆^{*1}、伊藤恵美子^{*1}、柴田大輔^{*1}、樋口隆昌^{*2}、永井伸夫^{*3}、下坂　誠^{*3}、岡崎光雄^{*3}
^{*1} 三井植物バイオ研究所、^{*2}日本大学農獣医学部、^{*3}信州大学応用生物科学科
Phenyalanine ammonia-lyase antisense gene transfer into tobacco by electroporation
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Makoto Shimosaka[*3], Mitsuo Okazaki[*3]
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Abstract: Phenylalanine ammonia-lyase (PAL) is the key enzyme in the formation of secondary metabolites including lignjn precursors. To control the production of lignin in plant cells, we constructed antisense genes using a PAL cDNA isolated from tobacco suspension cells. They were introduced into tobacco protoplasts by electroporation.

1991-116

ユーカリゲノムライブラリーの作成

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Construction of a genomic library from Eucalyptus (*E. saligna*)

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Mitsui Plant Biotechnology Research Institute

Abstract: We isolated genomic DNA from callus of Eucalyptus using CTAB (cetyltrimethyl- ammonium bromide). DNA fragments which was partially digested with Sau3Al were ligated with EMBL3. The DNAs were packaged into phase particles to obtain a genomic library, resulting one million recombinants.

1991-117

交雑ヤマナラシの宿主･ベクター系の構築及びアンチセンスRNA法によるリグニン生合成の解析

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Agrobacterium-mediated transformation of poplar and using antisense or sense gene fragment to study gene function of lignin biosynthesis

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Abstract: The long generation time of the tree means that genetic improvement by classical breeding is a slow process. Genetic engineering should be helpful in solving this problem. We have established a transformation system mediated binary vector of non-oncogenic *Agrobacterium tumefaciens* LBA4404 and applied this system to a analysis of the functional relationships of genes encoding enzymes of lignin biosynthesis pathway. So we introduced antisense and sense gene fragment into poplar hybrid clone and tobacco.

1991-118

リグニンモデル化合物分解酵素遺伝子のクローニング．XVIII. β-エーテラーゼ遺伝子の塩基配列とCα-デヒドロゲナーゼ遺伝子のクローニング

政井英司[*1]、窪田祥子[*1]、片山義博[*2]、川合伸也[*1]、山崎眞狩[*3]、諸星紀幸[*1]
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Cloning of the genes involved in degradation of lignin model compounds (XVII), Sequencing of the β-etherase gene and cloning of the Cα-dehydrogenase gene from *Pseudomonas paucimobilis* SYK-6

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Abstract: We have isolated *Pseudomonas paucimobilis* SYK-6 which could grow on various lignin dimeric compounds as a sole carbon source. Cleavage of β-aryl ether is the most important process in the lignin degradation because this linkage is the most abundant. We have already reported the detection of the activity of β-etherase in a cellular membrane fraction of *P.paucimobilis* SYK-6. This enzyme catalyzed the unique and reductive cleavage of arylglycerol-β-aryl ether (Cαcarbonyl type). Here, we report the sequencing of the β-etherase gene. This gene contains an open reading frame of 843bp and the molecular weight of deduced protein is 32,070. We named this gene ligE. The polypeptide expressed in *Escherichia coli* transformant was identified. In addition, we also found the Cα-dehydrogenase gene (ligD) for which the enzyme catalyzes the

Cα-dehydrogenation of arylglycero1-β-aryl ether (Cα alcohol type) in the 24kb Sal I fragment containing ligE.

1991-119

リグニンモデル化合物分解酵素遺伝子のクローニング（XIX）ビフェニル型化合物分解に関与する遺伝子の単離と解析

花城　薫[*1]、政井英司[*1]、片山義博[*2]、川合伸也[*1]、西川誠司[*1*3]、諸星紀幸[*1]

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Cloning of the genes involved in degradation of lignin model compounds (XIX)

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Abstract: *Pseudomonas paucimobilis* could grow on various lignin dimeric compounds as a sole carbon source. In particular, it is characteristic of this strain to degrade biphenyl compounds. We have already reported about the metabolism of biphenyl structure in lignin. Here we tried to isolate the gene involved in degradation of biphenyl compounds. We isolated the several mutants of *P. paucimobilis* SYK-6 deficient in degradation of compound (1) and (3). The gene which restore the wild's phenotype of mutants were isolated from cosmid genomic library of *P. paucimobilis* SYK-6.

1991-120

リグノスチルベン-α,β-ジオキシゲナーゼ産生遺伝子のクローニングと発現・同定

鴨田重裕、佐分義正

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Cloning, expression and identification of a lignostilbene-α□β-dioxygenase gene from *Pseudomonas paucimobilis* TMY1009

Shigehiro Kamoda, Yoshimasa Saburi

Faculty of Agriculture, the University of Tokyo,

Abstract: Lignostilbene-α□*β*-dioxygenases (LSDs) are the key enzyme responsible for the cleavage of the interphenyl Cα-Cβdouble bonds of stilbene type structure in the metabolism of dimeric lignin-related compounds by *Pseudomonas paucimobilis* TMY1009. Though LSD is similar to meta-cleavage dioxygenase in having nonheme iron, LSD is a new type dioxygenase which excels those in stability. To get the knowledge of the primary structure, it is one aim, cloning the gene encoding LSD has been done. The BamHI-KpnI fragment (8kbp) encoding a LSD gene was ligated in pUC19 at the same restriction enzyme site. *E.coli* JM109 carrying this plasmid produced LSD little. In this study, a SalI fragment (1.9kbp) was subcloned, the LSD gene on this fragment was expressed, and the products was identified.

1991-特別講演

リグニン化学における標識実験法

寺島典二

名古屋大学農学部

Invited lecture: Tracer method in lignin chemistry

Noritsugu Terashima

Faculty of Agriculture, Nagoya University

Abstract: Every wood chemist encounter serious difficulties in investigating the structure and reaction of lignin in the cell wall, because lignin is a structurally inhomogeneous macromolecule and it is impossible to isolate lignin in its unaltered state, or to depolymerize lignin into monomeric or oligomeric building units quantitatively. The nondestructive analysis of lignin labeled selectively with radioisotope or stable isotope at specific hydrogen and/or carbon gives useful information that is not obtained by any other methods. An outline and discussion are given of the recent advances in application of this technique to the studies on formation, structure and reaction of lignin in the cell wall.

1991-201

カワラタケが分泌するリグニン分解酵素とタンパク分解酵素の関係について —リグニン分解性ラッカーゼ (III) の糖鎖の役割

中村雅哉[*1]、西田篤実[*1]、吉武彰文[*2]、片山義博[*3]、飯村洋介[*3]、諸星紀幸[*3]

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Production of ligninolytic laccase and proteolytic enzymes in *Coriolus versicolor*

Masaya Nakamura[*1], Atsurni Nishida[*1], Akifumi Yoshitake[*2], Yoshihiro KaLayama[*3], Yousnke limura[*3], Noriyuki Morohoshi[*3]

[*1]Forestry and Forest Products Research Institute,[*2]Haechst Japan Ltd., [*2]Faculty of Agriculture, Tokyo University of Agriculture and Technology

Abstract: Ligninolytic laccase (laccase lII) from *Coriolus versicolorr* was known to be anionic glycoprotein. Structural analysis of this enzyme showed that laccase III contained at least four N-linked carbohydrate chains. Judging from the time course changes of laccase and protease activities in the culture fluids containing tunicamycin, these four carbohydrate chains had a protective function to maintain enzymatic activity under proteolytic condition. In particular, high proteolytic activity was identified in nitrogen starved culture filtrates. Partial characterization of proteases induced by nitrogen starvation stress is carrying out.

1991-202

リグニンパーオキシターゼの触媒サイクル

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東京大学農学部

Catalytic cycle of lignin peroxidase

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Abstract: The formation of super oxide during the lignin peroxidase (Li-P) reaction was confirmed by the reaction of super oxide with tetranitromethane (TNM). In the presence of H2O2, veratryl alcohol, Mn^{2+}, and TNM, trinitromethane anion was perhaps only one product by the Li-P reaction and veratraldehyde formation is not found. The same result was obtained when the above reaction was carried out under a nitrogen atmosphere. On the other hands, veratraldehyde was formed under the same condition as the above when *m*-chloroperbenzoic acid (CPBA) was used as an oxygen donor. Oxygen consumption which was observed during the Li-P reaction with veratryl alcohol, Mn^{2+}, arid H2O2 was not observed in the presence of CPBA instead of H2O2. These results strongly suggest that super oxide formation and oxygen uptake are independent of the substrate radicals.

1991-203

広葉樹培養細胞のリグニン生成とペルオキシターゼアイソザイムの基質特異性について（その 3）

堤　祐司、坂井克己

九州大学農学部

Lignin biosynthesis and substrate specificity of peroxidase isoenzymes with respect to syringyl and guaiacyl stracture in angiosperm tree callus cultures (III)

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Abstract: We have been investigating the possibility that substrate specificities of peroxidases can control syringyl/guaiacyl ratio of lignin in xylem tissues. It was found that the syringyl specific peroxidase (SyPO) was present in the ionically bound peroxidase (IPO) group extracted from callus culture of *Populus alba*. This SyPO isoenzyme specifically catalyzed the hydrogen peroxide- oxidation of syringyl substrates such as syringaldazine and 2,6-dimethoxyphenol but not the dehydrogenative polymerization of coniferyl alcohol. The IPO group from a *Populus alba* tree also exhibited the highest specificity for syringyl substrate among three peroxidase groups in both spring and summer. Whole peroxidase activities, especially syringyl oxidizing activity of IPO were decreased in summer.

1991-204

カワラタケによるリグニンモデル化合物のフェノール性水酸基のキシロース配糖化

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Xylosidation of phenolic hydroxyl group of lignin model compounds by *Coriolus versicolor*

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Abstract: In previous reports we showed that primary alcoholic hydroxyl groups of lignin model

compounds were bioconverted into their xylosides, in glucose media that were inoculated with *Coriolus versicolor*. In the present work, the xylosidation of phenolic hydroxyl group of lignin model compounds was investigated. When added to a culture of *C. versicolor*, methyl-guaiacol (MeG), a phenolic lignin model compounds, was bioconverted into 2-methoxy-4-methylphenyl-*β*-D-xyloside (MeG-Xyl). The formation of HG-Xyl was also observed in holocellulose media. When the cultivation was performed under nitrogen atmosphere to avoid the rapid consumption of MeG by laccase in the medium 28% of MeG was bioconverted into MeG-Xyl for 24 hours. Therefore, it can be concluded that not only alcoholic but phenolic hydroxyl group of lignin model compounds were transformed into their xylosides by *C. versicolor*. Furthermore,it was observed that the xyloside formation activity of *C. versicolor* was activated by the exogenous addition of phenolic compounds into the medium.

1991-205

バイオミメティツクフタロシアニン鉄錯体による β-*O*-4 型リグニンモデル化合物の酸化分解

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The biomimetic degradation of β-*O*-4 lignin model dimers by t-BuOH in the presence of octacarboxyphthalocyaninato-iron (III) catalyst

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Abstract: The biomimetic degradation of a β-*O*-4 lignin substructure model dirmer, 4-ethoxy- 3-methoxy-arylglycero1-β-vanillyl alcohol ether (I), by *tert*-butylhydroperoxide in the presence of octacarboxyphthalocyaninato-iron (III) (Fe(III)Pc) was investigated. The substrate (I) Was oxidatively degraded by catalysis of Fe(III)Pc in aqueous solution at pH 3 at room temperature. This catalyst was found to mimic a lignin peroxidase (LiP) activity, yielding both C-C bond cleavage and aromatic ring opening products derived from β-*O*-4 substrate (I). The β-*O*-4 dimer (II) formed from substrate (I) was also degraded to give C-C bond cleavage products. vanillin and 4-O-ethylvanillic acid, in alkaline solution at room temperature.

1991-206

硫酸触媒を用いた広葉樹材の常圧酢酸パルプ化 —高分子リグニンの利用研究のための多量リグニン簡易分離法としての評価

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Pulping of hardwoods at atmospheric pressure with aqueous acetic acid containing a small amount of sulfuric acid -Characterization of resulting acetic acid lignins as raw materials for utilization studeis of polymeric lignins

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Abstract: Acetic acid lignins (AWL) can be produced without tedious operation and in quantity from the reaction solution obtained by atmospheric pulping with aqueous acetic acid containing a small amount of sulfuric acid. Therefore, the lignins may be used in the utilization studies of lignins with large quantities, if they are modified less greatly during the pulping. To determine the possibility, the chemical structure of AWLs was characterized by the elemental analysis, analysis of functional groups by ^{1}H-NMR and other methods, several degradation procedures average molecular weights and so forth.

1991-207

広葉樹クラフトパルプ中のキシランとリグニンの関係

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Characterization of xylan and lignin in hardwood kraft pulp

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Keywods: 広葉樹クラフトパルプ・ヘミセルロース・キシラン・リグニン・カッパー価・未晒パルプ
hardwood kraft pulp, hemicellulose, xylan, lignin, kappa number, unbleached pulp

Abstract: Relation between lignin and xylan in hardwood kraft pulp was investigated. From the unbleached pulp and oxygen delignified pulp, xylan ms isolated, and then lignin contents in these fractions, xylans, extracted pulps and extraction liquors were measured by the use of Kappa number method. In the case

of chlorine and alkali treated pulp and bleached pulp, chlorine contents of the fractions were measured instead of the lignin contents. These results show that about half of the residual lignin in kraft pulp exists in xylan fraction. It may suggest that the lignin should be linked with xylan chemically.

1991-208

酸素・アルカリ脱リグニン過程における炭水化物の崩壊機構（1）糖の分解に及ぼすリグニンの影響についてのモデル実験

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Effects of lignin structure on carbohydrate degradation during oxygen bleaching

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Abstract: Methyl β-D-glucopyranoside (MeβG) was treated with oxygen under an oxygen bleaching condition in the presence or absence of various types of lignin model compounds as well as waste liquor lignin obtained by oxygen bleaching of pine kraft pulp. Then lignin model compounds were absent, MeβG wasn't degraded at all. ln the presence of phenolic lignin compounds without α-carbonyl group, MeβG was degraded to a significant extent, which was proportional to the amount of added model compounds. Whereas the whole waste liquor lignin didn't show any degradation effect, its high molecular weight fraction showed strong effect on the MeβG degradation.

1991-209

酸素酸化パルプ化による稲わらリグニンの変化（1）

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Variation of rice straw lignin with NaOH-O2 pulping (I)

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Abstract: Rice straw is readily pulped by oxygen oxidation after alkali soaking. To investigate changes of lignin and polysaccharides during the gulping, waste liquors of soaking and pulping were subjected to a series of extraction of acid-precipitated solid (AP), acid-soluble lignin (ASL) and polysaccharides, and then were analyzed. Because of the existence of nitrogen in the straw, all the products contained nitrogen. Purified AP from soaking waste liquor did not contain nitrogen, but pulped lignin still retained high content of nitrogen, nearly equal to 5 times that of the straw. It also showed that the lignin subject to oxidation was degraded to a great extent.

1991-210

アルカリ・アルコール・アントラキノン蒸解について

阿部善作

九州大学農学部

Alkali-alcohol-anthraquinone pulping

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Abstract: This investigation was carried out to obtain better understandins of alkali-alcohol-anthraquinone pupling. It was compared with other pulpings ; alkali-alcohol pulping, alkali- anthraquinone pulping, and kraft pulping. As the results were shown in Fig.1, alkali-alcohol- anthraquinone pulping can produce unbleached pulp of the lowest lignin content at high pulp yield.

1991-211

アルコール・バイサルファイト処理によるリグニンモデル化合物の β-O-4 結合開裂反応の特徴（その 2）

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Characteristics of the β-*O*-4 bond cleavage reaction during an alcohol-bisulfite treatment of lignin model compounds (II)

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Factllty of Agriculture, Kyushu University

Abstract: Lignin model compounds shown in Fig.1 were synthesized and subjected to alcohol- bisulfite (AB) treatment and alcohol-phosphate buffer (AP) treatment at 160ºC for 30 and 60 min. Substituents at the position para to the β-*O*-4 bond in the ring a provided no large influence on yields of isoeugenol and phenols derived from the ring B that were produced by the β-*O*-4 bond cleavage in the AB treatment. Recovery of starting materials after the AB treatment was about the same as those after the AP treatment of the sane compounds. We now presume that the β-*O*-4 bonds in phenolic lignin units are cleaved homolytically during the AB treatment. Radical intermediates formed by the homolysis may be stabilized by a rapid electron transfer from bisulfite anions and/or bisulfite radicals.

1991-212

リグニンのメカノケミストリー（XII）　(5,5’)-(β-*O*-4)型三量体リグニンモデル化合物の合成とそのメカノケミストリー

伊藤和貴、住本昌之
九州大学農学部

Mechanochemistry of lignin (XII), -Synthesis and mechanochemical conversions of (5-5')-(β-*O*-4) type of trimer lignin model compound

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Abstract: Trials for the improved method of synthesis of (5-5')-(β-*O*-4) type of trimeric lignin model compounds (I) and (II) were made by application of benzyltri-n-butylammonium bromide as a phase-transfer catalyst. Mechanochemical treatments of the model compound (I) with VBM and CBM furnished a (5-5')-β-*O*-4) type of trimer having a para-carbonyl pheno1 (III), and a pair of oxidation products of 3-methoxy-5-substituted para-benzoquinone (IV), and 2-(2-methoxy- phenoxy)-3-hydroxypropionic acid (V), and the other product (VI).

1991-213

リグニンのメカノケミストリー（XIII） Veratrylglycerol-β-syringylaldehyde etherの反応とその機構について

呉　宗華、住本昌之
九州大学農学部

Mechanochemistry of lignin (XIII), Mechanochemical reductions and mechanisms of veratrylglycerol-β-syringaldehyde ether

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Abstract: To clarify the mechanochemical reaction mechanisms of veratrylglycerol-β-syringaldehyde ether (M), comparative treatments of the compound (M) were made with VBM under nitrogen or air. Treatments under nitrogen resulted in the significant decrease in the yields of 3,5- dimethoxy-*p*-hydroquinone and 3,5-dimethoxy-*p*-benzoquinone but a little increase in the yields of syringaldehyde compared to those under air. This strongly suggested that •O2H radical is formed in the aqueous media to react with syringaldehyde moiety. Addition of normal paraffin alcohols served as •OH radical scavengers showed that the mechanochemical reactions were heavily retarded. The formation of adduct of phthalic hydrazide with •OH radical fully confirmed the presence of •OH radical in the aqueous media of VBM during the treatments. Likely to those in the media of super sound, the aqueous media of mechanical pulping produces •O2H, •H, and •OH radicals to convert mainly lignin.

1991-214

*Phanerochaete chrysosporium*による塩素化フェノール類の代謝 (2) 塩素置換位置とフェノール性水酸基 のメチル化の影響

小野克正、桃原郁夫、松本雄二、石津　敦
東京大学農学部

Metabolism of chlorinated phenols by *Phanerochaete chrysosporium*

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Abstrsct: When chloroguaiacols were t.rented with lignin peroxidase (Li-P) in the presence of veratryl alcohol (VA), they were oxidized easily and oxidation of VA does not proceed until the reaction of chloroguaiaco18 was completed, indicating that VA oxidation is strongly inhibited by chloroguaiacols. On the

other hand, chloroveratrol did not show any inhibiting effect on VA oxidation and, even under a very low H2O2 concentration, spectral change was not observed in the absence of VA. These results coincide with the observation that metabolism of chlorophenols by *P. chrysosporium* are prohibited by methylation reaction which is apparently active throughout the life time of this fungus.

1991-215

リグニン分解菌（IZU−154 株）によるクラフトパルプ漂白廃液の処理

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Decolorization of kraft bleaching effluent by the lignin-degrading fungus IZD-154
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Abstract: In the previous reports, we showed that biomechanical pulping and biobleaching were successfully performed by the treatment with a hyperligninolytic fungus IZU-154. In the present work, we tried to decolorize the bleaching effluent from an alkaline-extraction stage (E1) by the fungus IZU-154. To establish an effective color removal process, various cultivation parameters of IZU-154 and treatment conditions of E1 effluent with the fungus were investigated. Under the best conditions employed here, a treatment with IZU-154 for 24 hours in the presence of a small amount of glucose resulted in 95% reduction of color of an undiluted E1 effluent containing 7,500 color unit. On the other hand, when the effluent was treated with *Phanerochaete chrysosporium* and *Coriolus versicolor* under the same conditions, only 58% and 19% of the color were removed after a 48-hour incubation. The elucidation of the mechanism of color reduction by the fungus IZU-154 is now in progress.

1991-216

機械パルプの微生物処理に関する研究（VIII）光退色におよぼすカルボニル基の影響

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Studies on biological treatment of mechanical pulps (VIII)
Effect of carbonyl groups on light-induced color reversion of mechanical pulps
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Abstract: The effect of carbonyl groups on light-induced color reversion of mechanical pulps was examined. For the first time, reduction of seven model compounds containing α-carbonyl group with KBH4 accompanied with or without phase transfer catalyst (PTC) was conducted to find out an effective reduction method for the groups. The model compounds could not be reduced with KBH4 only, however, the reduction of the model compounds with KBH4 proceeded significantly by addition of small amount of PTC. Based on the results obtained from the model experiments, mechanical pulps were treated with KBH4 accompanied with PTC before and after bleaching. Light-induced color reversion of bleached groundwood pulp (GP) was suppressed 33 to 44% by pretreatment of GP with KBH4 accompanied with PTC. However, in the case of thermomechanical pulp (TMP) and pressurized groundwood pulp (PGW), the depression of the color reversion was 11 to 19% and11to 23%, respectively, to that of the untreated pulp. It is suggested that the effect of carbonyl groups on the color reversion of mechanical pulps is not so high.

1991-217

リグノセルロースのリン酸エステル化によるヒドロゲル化（第 3 報）吸水性に及ぼすリグニンの影響

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Hydrogelation of lignocellulosic materials by phosphorylation (III), Effect of lignin content on the water absorbency
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Hokkaido Forest Products Research Institute

Abstract: To investigate the effect of pretreatment with acidic sodium chlorite on swelling behavior of phosphorylated lignocellulosic materials, chlorite treated wood meals containing various amounts of lignin were prepared. In the early stage of delignification, the procedure was quite selective in removing lignin, and no significant change in carbohydrate content was observed. Water absorbency of chlorite treated wood meals followed by phosphorylation with phosphoric acid and urea rapidly increased with increasing degree of delignification during the first 65 %. When wood meals were treated with chlorite three times, maximum water absorbency (141 gH2O/g) gas obtained. Degree of delignification of the treated wood meals was 65 %, and their carboxyl group content was maximum (0.48 mmol/g). These results indicate that delignification and carboxyl group content of wood meals play an important role in hydrogelation of the phosphorylated products.

1991-218
リグニンのヒドロキシアルキル化（I）リグニンとグリセロールの反応
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Hydroxyalkylation of lignin (I), Reaction of lignin with glycerol
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Abstract: In the case of the preparation of polyurethane from lignin, it is necessary to modify lignins to the derivatives which possess high reactivity to isocyanates. Then in this study, we tried to introduce alcoholic hydroxyl groups into lignin model compounds. Three kinds of lignin model compounds (phenol, guaiacol, syringol) were treated with glycerol α-monochlorohydrin. The products having alcoholic hydroxyl groups were identified based on the NMR and MS spectra. The reaction of these modified model compounds with isocyanates are now carried on.

1991-219
Synthesis and properties of lignin based epoxy resins
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Abstract: Lignin from steam-exploded yellow poplar wood was chain-extended by hydroxypropylation of the hydroxyl groups. Depending on the amount of propylene oxide used chain-ext:ended hydroxypropyl lignins (CEHPL) with various polyether chain lengths were obtained which had a wide range of viscoelastlc properties. Endcapplng of the poly (propylene oxide) segments with ethylene oxide and subsequent epoxidation with epichlorohydrin yielded segmented, star-like epoxy resins. Fractionation by precipitation in aceton:hexane solvent systems was carried out to obtain poly (propylene oxide) homopolymer free resins with different molecular weights and narrow molecular weight distributions. Curing of these compounds with m-PDA yielded materials which ranged from elastomers to rigid solids, depending on the molecular weight and the level of chain-extension. Also their mechanical properties showed a wide variation whereby the short chain-extended, high molecular weight materials exhibited strengths and moduli in the same order as those of a commercial DGEBA based resin.

1991-220
リグノセルロース系ポリウレタン分子複合材料の力学的性質
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Molecular composites consisting of polyurethanes from lignocellulosics
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Abstract: Solvolysis lignin and wood tar were used in the preparation of molecular composites consisting of paper and polyurethane (PU). The composites of filter paper (FP)-solvolysis lignin (SL)-diphenylmethanediisocyanate (MDI) (FP-SL-MDI), FP-SL-polypropyleneglycol (PPG)-MDI (FP-SL-PPG-MDI), FP-wood tar (WT)-MDI (FP-WT-MDI) and FP-WT-PPG-MDl systems were prepared. Mechanical properties of these composites were investigated by a tensile test machine. The tensile strength of the composites of FP-WT-MDI system increased with increasing the amount of PU/FP (g/g). The maximum stress of the composites was five times higher than that of filter paper. It is found that PPG acts as a soft segment in those systems.

1991-221
リグニン分解物を原料とする液晶性全芳香族ポリエーテルの合成と熱的性質
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Synthesis and thermal analysis of liquid crystalline aromatic polyethers derived from degradation products of lignin

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Abstract: Aromatic polyethers were synthesized by the condensation of 4..4'-difluoro-3,3'-dinitro-benzophenone with potassium salts of hydroquinone derivatives such as 2.5-dimethoxy- hydroquinone, 2,5-dimethylhydroquinone and hydroquinone. Average molecular weights of the obtained polyethers were in the order of 10^4. Thermal properties of the polyethers were studied by thermogravimetry and differential scanning calorimetry. Polyethers started to decompose at ca. 250 ºC and their glass transition temperatures were in the range of 140 ºC to 189 ºC. The liquid crystalline phase of *p*-chlorophenol solutions of polyethers was observed using a polarizing microscope.

1991-222

バクテリアセルロース製造における炭素源としての低分子酸・アルコール類

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Evaluation of low molecular acids and alcohols as the carbon source for the production of bacterial cellulose

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Abstract: Low molecular nine acids and six alcohols were evaluated as the carbon source for the production of bacterial cellulose. A bacteria, *Acetobacter xylinum* ATCC 10245 under the Hestrim-Schram's mediun system was used for the evaluation. Among alcohols, glycerol gave the best cellulose yield (152% ; based on the membrane yield from glucose) and the inositol (89%) followed. Among the acids, lactic acid save the best yield (71%) and the pH of the culture medium increased from 6.0 to 9.2. Acetic acid gave a little cellulose yield (11.7%) but the pH of the culture medium went up to 7.95 as in the case of lactic acid.

1991-特別講演

リグニンのメカノケミストリーとパルプ漂白

住本昌之

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Mechanochemistry of lignin in pulping and its relation to pulp bleaching

Masashi Sumimoto

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Abstract: Mechanochenical treatments of various types of lignin model compounds with CAM, VBM, and laboratory refiner disclosed that O2H, OH, and H radicals were produced in the aqueous media of mechanical pulping, similarly to those in the aqueous media of super sound. Effective attack of such radicals to either syringyl glycerol-*β*-guaiacyl ether or (5-5')-biphenyl type of model compound hawingα-carbinol furnished the corresponding para-carbonyl phenol, and 3-methoxy-5- substituted *p*-benzoquinone, respectiyely. Furthermore. mehanical treatnent of a 5-substituted-*p*- carbonyl phenol ether produced a pair of chromophore, p-benzoquinone and a leucochromophore, *p*-hydroquinone. Alkaline H2O2 bleaching destructs most of the chromophor but the leucochromo- phores, which are believed to be the major cause of color reversion of bleached mechanical pulp.

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1992-101
担子菌 *Coriolus versicolor* によるリグニン分解機構の解析
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Elucidation of lignin biodegradation mechanism by basidiomycete *Coriolus versicolor*
Yousuke Iimura, Shinya Kawai, Yoshihiro Katayama, Noriyuki Morohoshi
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Abstract: A white-rot basidiomycete, *Coriolus versicolor* secrets a number of extracellular laccases. ln polymeric lignin metabolism by *C. versicolor* laccase activity was closely related to the accumulation of water soluble intermediates. In this fungus, a multitude of laccase gene related DNA sequence was observed. We have cloned and sequenced a gene coding for the ligninolytic Laccase lIl and homologus laccases of *C. versicolor*.

1992-102
白色腐朽菌のリグニン分解に関与する酵素系に関する研究（I）自然界より分離したリグニン分解菌のリグニン分解特性及び菌体外酵素活性
平井浩文、近藤隆一郎、坂井克己
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Studies on ligninolytic enzymes of white-rot fungi. I. Lignin-degrading characteristic and extracellular enzyme activities of new isolates of white-rot fungi
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Abstract: We previously reported that new isolates of white-rot fungi, YK-472 and YE-624, showed much higher ligninolytic activity and selectivity in beech-wood lignin than typical lignin- degrading fungi, *Phanerochaete chrysosporium* and *Coriolus versicolor*. In the present work, we investigated their lignin-degrading characteristic and extracellular enzyme activity. The fungi YK-472 and YK-624 degraded birch dioxane lignin and residual lignin in unbleached kraft pulp (UKP) much higher than *P. chrysosporium* and *C. versicolor*. During fungal treatment of beech wood meals, the fungus YK-624 which degraded beech-wood lignin, showed much higher activity of extracellular peroxidase in the medium than *P. chrysosporium*.

1992-103
Phanerochaete chrysosporium の生産するセロビオース脱水素酵素の性質とリグノセルロース生分解におけるその役割
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Cellobiose dehydrogenases from *Phanerochaete chrysosprium*, Enzymatic properties and functions in lignocellulose biodegradation
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Abstract: In relation to ligncellulose biodegradation by *Phanerochaete chrysosporium*, enzymatic properties of cellobiose oxidase (CBO) and cellobiose : quinone oxidoreductase (CBQ), especially the specificity of electron acceptors for these enzymes, were investigated. CBO can reduce quinones as yell as CBQ in the presence of cellobiose. FAD is a common prosthetic group for both enzyme. Therefore, these reductions are conducted by FAD. Atmospheric oxygen is a poor electron acceptor for both CBO and CBQ. In contrast, cytochrome c is utilized as an effective electron acceptor by CBO. The pH dependence experiment and the stopped flow analysis suggest that the reduction of cytochrome c is depending on the function of heme prosthetic group in CBO indicating that cytochrone c is a most possible electron acceptor for CBO in vivo system. The amount of CBO in the cellulolytic culture increases in the course of the fungal growth. Therefore all of these results suggests that CBO participates in cellulose biodegradation rather than lignin biodegradation. On the other hand, CBQ produces in the later stage of the cellulolytic culture like as a secondary metabolite. Therefore, CBQ has less importance in cellulose bidegradation.

1992-104

Phanerochaete chrysosporium の芳香環開裂酵素について

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Aromatic ring cleavage enzyme from *Phanerochaete chrysosporium*

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Forestry and Forest Products Research Institute

Abstract: In an investigation of vanillic acid metabolism by *Phanerochaete chrysosporium*, aromatic ring cleavage enzyme is very unstable so the purification of the enzyme is very difficult. In this time, we succeeded in the purification of hydoxyquinol 1,2-dioxygenase and clarified the some properties. The native molecular weight of this enzyme is 94,000 Dalton and the subunit molecular weight are 40,000 and 52,.000 Dalton (by SDS-Page). The enzyme is inactivated with Fe^{2+} and -SH chelator. Optimum pH is 6.0-6.5 and pH stability is 6.5-7.5 in phosphate buffer.

1992-105

マツノカタワタケによる β-O-4 型リグニンサブストラクチヤーモデル二量体の分解

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Degradation of β-O-4 lignin substructure model dimers by *Cryptoderma pini*

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Abstract: Degradation of a non-phenolic (1-(4-ethoxy-3-methoxyphenyl)-2-(2,6-di-methoxy-phenoxy)-1,3-propanediol (I)) and a phenolic (1-(4-hydroxy-3-methoxy-phenyl)-2-(2,6-dimethoxy-phenoxy)-1,3-propanediol (II)) β-O-4 lignin substructure model diners by the intact cells of *Cryptoderma pini*, and activities of lignin-degrading enzymes in the extracellular culture fluid of the fungus were investigated. In the degradation of substrate (I) by the fungus, degradation products were formed via *O*-C4 cleavage and β-etherified aromatic ring opening. On the other hand, substrate (II) was degraded via alkyl-aryl cleavage. In addition, activities of laccase and Mn(II)- dependent peroxidase were detected in the extracellular fluid of the fungus culture.

1992-106

有機溶媒中におけるペルオキシダーゼの反応

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Reaction of peroxidase in organic solvents

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Abstract: Horseradish peroxidase (HRP) was modified with methoxypolyethylene glycol- succinimidyl succinate (MPSS. MW 5000) to dissolve in organic solvent. The modified HRP retained over 85% of the original activity in potassium phosphate buffer, and its Km value and Vmax were about the same as those of native enzyme. Similarly, lignin peroxidase (LiP) was purified from culture filtrate of *Phanerochaete chrysosporium*, and modified with MPSS under neutral pH condition. The hydrophobically modified HRP and LiP were soluble in benzene. Reaction of both modified peroxidases in organic solvent is reported_

1992-107

透析膜法によるシナピルアルコールの酵素的脱水素重合

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岐阜大学農学部

Enzymatically dehydrogenative polynerization of sinapyl alcohol by dialysis membrane method

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Abstract: In a plant cell wall, a lignin was deposited in the matrix of polysaccharides through the lignification process. To prepare the closer model of a native lignin, sinapyl alcohol was polymerized with horseradish peroxidase/H2O2 in the presence of xylan or pectin by dialysis membrane method, and their chemical structures were investigated. As a result, the ratio of acidolysis monomers to syringaresinol was

determined about 20 :1 in xylan and about 10 :1 in pectin. Further, there was a little benzyl phenyl ether in dehydrogenation polymer (DHP) fraction of the LCC/xylan. The degree of polymerization of the DHP was decided to be twenty-five by the determination of phenolic hydroxyl group and yield of acidolysis monomers. Dehydrogenative polymerization of monolignols by the dialysis membrane method would sufficiently simulate the lignification process in a plant cell wall.

1992-108

抗ウイルス活性を有する水溶性腐朽バガスリグニンの化学構造

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Characterization of antiviral water-soluble lignin from bagasse degraded by *Lentinus edodes*

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Abstract: We characterized water soluble lignin (WSL) which is responsible for antiviral activity of lignin complex (LC) extracted from bagasse degraded by *Lentinus edodes*. The results of potassium permanganate oxidation show that WSL contains larger amounts of condensed type structures than MWL. However, the methoxyl content of WSL was lower than that of MWL. Thus. the new evidence is that the quantities of benzene rings in WSL were obviously reduced, which suggests that bagasse lignin were modified to those rich in ring opening or quinone moieties during the decay process. The hydrolysis of WSL with aqueous sodium hydroxide yielded oxalic acid and formic acid, which indicates WSL contains oxalate and formate esters possibly derived from the aromatic-ring opening structures.

1992-109

リグニン構造単位の選択的標識に関する研究（I）

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Studies on the selective radio-labeling of lignin structural units in tree xylem (I)

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Abstract: For the selective labeling of lignin structural units, monolignol glucosides are considered as suitable precursors. However, during a long term metabolism after the administration of these labeled precursors, a certain proportion of interconversion between each units (*p*-hydroxy- phenyl, guaiacyl, syringyl) was often observed. To avoid this conversion, γ-hydrogens labeled monolignol glucosides were employed. If the conversions occur, these γ-hydrogens must be released because in lignin biosynthetic pathway, it is considered that OMT functions for *p*-hydroxy cinnamic acids which has no γ-hydrogens. In this study, γ-hydrogens in monolignol glucosides were labeled with deuteriums, and their behavior during the dehydrogenated polymerization was investigated using the preparing DHP. It was found the γ-hydrogens were stable through the reaction.

1992-110

リグニン構造単位の選択的標識に関する研究（II）

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Studies on the selective radio-labeling of lignin structural units in tree xylem (II)

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Abstract: To achieve the selective labeling of lignin structural units, the γ-position of lignin C6-C3 units was labeled by the administration of γ–^{3}H labeled monolignol glucosides to the plants. The newly formed lignin was degraded to C6-C3 units by thioacidolysis, and the radioactivity of degradative products (derived from guaiacyl, syringyl units) were measured. The perfectly selective labeling was expected, however, a considerable proportion of interconversion was observed in the angiospermous trees administered with *p*-glucocoumary lalcohol and coniferin. When syringin was administered, little conversion was observed. These suggest that new route (or mechanism) of interconversion which does not pass the cinnamic acids exists in the lignin biosynthesis.

1992-111

広葉樹樹幹先端部における木部分化とリグニン不均一形成に関する研究

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Studies on the heterogeneous formation of lignin in the elongating shoot of *Magnolia kobus*

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Abstract: The differences in lignification between the vessel of primary xylem and that of secondary xylem are discussed. The vessels of primary xylem of *Magnolia kobus* have thickened spiral secondary wall. This secondary wall lignifies in the early stage of shoot formation. However, the lignification of the compound middle lamella is fairly delayed. This pattern of lignification is quite different from that of secondary xylem. In addition, surprisingly, it was found that the vessel of primary xylem with lignified secondary wall dramatically elongated (approximately 3.5 fold) like a spring coil during the growth of the shoot.

1992-112

雲南省産カエデ属数種のリグニンの分布

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Distribution of lignins on the genus *Acer* in Yunnan

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Abstract: Distribution of lignins of 5 species on the Genus *Acer* in Yunnan was investigated by Mäule reaction, ultraviolet microscopy and Klason method. Absorption spectra of Mäule reaction show that all 5 species were syringyl lignin rich in all elements.

1992-113

Forsythia sp. のリグナン生合成の初発段階を触媒する(＋)−ピノレジノールシンターゼ

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(+)-Pinoresinol synthase: The first enzymatic step committed to lignan biosynthesis in the *Forsythia sp*.

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Abstract: Detailed fractionation studies have determined that in the insoluble residue from *Forsythia sp* (*F. suspensa* and *F. intermedia*) there exists a coniferyl alcohol coupling enzyme which catalyzes preferential formation of (+)-pinoresinol in the absence of cofactors. When NAD and malate were supplied, the stereoselectivity of the coupling reaction was enhanced. Sinapyl alcohol does not serve as a substrate for this enzyme i.e. in this case stereoselective coupling does not occur. Thus, lignan biosynthesis in the *Forsythia sp.* is initiated by the coupling of the two coniferyl alcohol molecules to give (+)-pinoresinol, this being the first isolable product of stereoselective coupling.

1992-114

(＋)−ピノレジノールのエナンチオ特異的還元

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Enantiospecific reduction of (+)-pinoresinol

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Abstract: Time-course experiments using *Forsythia intermedia* cell-free extracts, incubated with coniferyl alcohol in the presence of NADPH and H2O2, revealed that formation of (-)-secoiso- lariciresinol was linear over the time period examined. But, these crude cell-free extracts also catalyzed formation of (±)-pinoresinols as the initial coupling products. The (+)-enantiomer was then selectively depleted, as a function

of time, from the incubation mixture, with concomitant formation of (-)-secoisolariciresinol. By contrast, the (-)-antipode remained unchanged. Next, the cell-free extracts were incubated with (±) and (+)-pinoresinols. Formation of (-)-secoisolarici- resinol from the (+)-antipode was again observed, but only required NADPH as a cofactor.

1992-115

Lignan biogenesis：Towards elucidating ragio- and enantiospecific methylation/glucosylation transformations beyond matairesinol

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Abstract: Since the pathway from (+)-pinoresino[to (-)-matairesinol in *Forsythia intermedia* is characterized by highly enantioselective enzymatic conversions, it was of interest to establish whether comparable enantioselectivity was extended into arctigenin/arctiin formation, and if the apparent regiospecificity of methylation was controlled at this stage. But, in contrast to previous enantiosesective enzymatic steps affording (-)-matairesinol, it was found that both (+)- and (-)-antipodes of matairesinol served as substrates for methylation -with the naturally occurring (-)-enantiomer slightly preferred. Surprisingly, the major enzymatic products were (+)- and (-)-isoarctigenins rather than the naturally occurring regio-isomer, (-)-arctigenin. Thus, *O*-methyLation of matairesinol was neither enantioselective or regiospecific. Further, only monomethylation was observed, since no evidence for dimethyl matairesinol formation occurred. Taken together, it is proposed that regiospecific methylation of matairesinol does not proceed to give arctigenin directly. Instead, regiospecific glucosylation is presumed to first occur to afford matairesinoside. Subsequent methylation affords arctiin, which is converted into arctigenin via action of a β-glucosidase.

1992-116

Forsythia koreana のリグナン生合成酵素

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Enantioselective lignan formation by cell-free extracts of *Forsythia koreana*

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Abstract: Cell-free extracts from *Forsythia koreana* catalyzed the formation of (-)-secoiso- lariciresinol, as well as (-)-pinoresinol and (-)-lariciresmol. When incubated with coniferyl alcohol in the presence of NADPH and H2O2. The extracts also catalyzed the formation of (-)-secoisolarici- resinol from (±)-lariciresinol. The mechanisms of the enantioselective (-)-secoisolariciresinol formation are discussed.

1992-117

ウド（*Aralia coradata*）シンナミルアルコールデヒドロゲナーゼ cDNA の単離および解析

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Isolation and characterization of a cDNA encoding cinnamyl alcohol dehydrogenase from *Aralia cordata*

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Abstract: We isolated a full-length cDNA clone encoding cinnamyl alcohol dehydrogenase (CAD; EC1.1.1.195) from *Aralia cordata* by oligonucleotide-screening derived from amino acid sequence of *A. cordata* CAD protein. The cDNA clone comprised a open reading frame of 1080 base pairs. The partial amino acid sequences of peptides isolated from the purified CAD of *A. cordata* were found in that deduced from the cDNA nucleotide sequence. This showed the cDNA clone encodes CAD of *A. cordata.*

1992-118

樹木フエニルプロパノイド系生合成酵素遺伝子群の単難・解析

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Isolation arid analysis of the genes encoding the enzymes for phenylpropanoids biosyrlthesis in woody plants

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Abstract: We use *Populus kitakamiensis* as a model for analysis of lignification in woody plants. For the analysis of gene regulation in lignification process and moleculer breeding of lignin less tree, it is necessary to isolate the genes encoding enzymes for lignin biosynthesis. We isolated some phenylalanine ammonia-lyase, *O*-methyltransferase, and peroxidase genes from the poplar genome. And some of them were characterized.

1992-119

アンチセンス RNA 法を用いた樹木の分子育種

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Molecular breeding of woody plants by using antisense RNA method

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Abstract: Cells of the hybrid poplar (*Populus kitakamiensis*) were transfomed by *Agrobacterium*-mediated gene transfer and regenerated into plants from the transformed calli. T-DNA of plasmid DNA, pBI121, bearing marker genes encoding beta-glucronidase (GUS) and neomycin phospho- transferase (NPTII) were introduced by non-oncogenic *Agrobacterium tumefaciens* LBA4404 using leaf disk method. The transformed cells grew into calli on the selective medium containing kanamycin and calli regenerated into plants. The kanamycin resistant plants were analysed by Southern blot hybridization and a fluorometric assay for GUS. All kanamycin resistant plants had two marker genes and were confined as transformants. And sense or antisense genes for phenylalanine ammonia-lyase or peroxidase derived from the poplar genome were introduced into the poplar and the transfomants were regenerated into plants.

1992-120

リグニンビフエニル型化合物の分解酵素遺伝子の解析

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Cloning of the genes involved in degradation of biphenyl structure of lignin compounds

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Abstract: *Pseudomonas paucimobilis* SYK-6 is able to grow on DDVA (biphenyl structure of lignin) as a sole carbon source. We have already reported that the metabolism of DDVA proceeds via intermediates, OH-DDVA, 5-carboxyvanillate. The first step in the catabolism of DDVA by SYK-6 is the demethylation of DDVA to OH-DDVA. In this study we report, using as a host strain for the nitrosoguanidine mutant NT1 which was isolated for loss of the ability to use DDVA as a carbon source, we isolated the genes involved in DDVA catabolism.

1992-121

β-アリールエーテル開裂酵素遺伝子群の機能と構造

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Structures and functions of the genes involved in the cleavage of β-aryl ether

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Abstract: *Pseudomonas paucimobilis* SYK-6 is able to assimilate various types of dimeric lignin compounds. Cleavage of arylglycerol-β-aryl ether is essential in the lignin degradation. We have already characterized the β-etherase gene (*ligE*). Here, we isolated and characterized the Cα- dehydrogenase gene (*ligD*). Cα-dehydrogenase catalyzes the oxidation of arylglycerol-β-aryl ether and this process produces the specific

substrate for β-etherase. Homology search showed that ligD had a homology with ribitol dehydrogenase family. Mapping and sequencing analysis indicated *ligD* and *ligE* were separated by an open reading frame encoding another β-etherase gene (*ligF*). β-etherase activity of ligF expressed in *Escherichia coli* was more than100 times as high as that of ligE. We found that ligF was homologous to glutathione S-transferase. Drastic acceleration of β-etherase activity was observed in the reaction mixture including ligF by addition of glutathione.

1992-201

リグニンの熱分解ガスクロマトグラフィー（第 4 報）単難リグニンの熱分解ガスクロマトグラフィ

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Analysis of lignin by pyrolysis-gas chromatography (IV), Pyrolysis-gas chromatography of sugi wood, its lignin preparations and synthetic lignin

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Abstract: Curie-point pyrolysis of wood and several isolated lignins from sugi (*Cryptomeria japonica* D. Don) and synthetic lignin was performed. Pyrolysis products were analyzed by GC and GC/MS. Total yields of selected pyrolysis products were ordered as follows: wood > DHP > MWL > alcohol bisulfite lignin >HC1-lignin > DL >> KL. Py-GC of lignin gave different product distribution profiles from that of wood meal; coniferyl alcohol was the most abundant lignin marker product in the wood pyrolysate, and a minor product in its lignin pyrolysate. These findings showed that analytical pyrolysis data may help in achieving a better understanding of the structural change of lignin.

1992-202

リグニンのメカノケミストリー（XVI）　グアイアシルグリセロール-β-グアイアシルエーテルのメカノケミストリー

伊藤和貴、住本昌之、田中浩堆
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Mechcanochemistry of lignin (XVI), Mechanochemical conversions of guaiacylglycerol-β-guaiacyl ether

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Mechanochernical conversions of vanillylalcohol I, α-methyl vanillylalcohol II, and guaiasylglycerol-β-guaiacyl ether IV were investigated. Two types of conversions occurred by the treatment of compound IV with VBM. The major reaction furnished firstly the corresponding *p*-carbonyl phenol 4, which afforded six products similarly to the case of syringylglycerol-β-guaiacyl ether, but strangely included 2-methoxy-*p*-hydroquinone 5. The minor reaction involved Abstraction of phenolic H atom followed by dimerization to give compound 10 which was oxidized further via compound 11 to 12.

1992-203

爆砕処理よるリグニンの分解機構の解明（VI）シリンギル型リグニンモデル化合物の水蒸気処理

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Degradation mechanism of lignin by steam explosion (Vl), - Steam treatment of syringyl type of lignin model compound

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Abstract. ln order to explain the degradation mechanism of lignin by steam explosion, syringyl-glycerol-β-sinapylalcohol ether (SS) was used in the present study. This model compound was subjected to the steam treatment, 230 ºC, 2.9 MPa for 4 min. Steam treatment of S-DHP and S-LCC was also subjected to the steam treatment. The major degradation product obtained from steamed SS was syringaresinol. Other products found were sinapyl alcohol, sinapaldehyde, dehydrosinapyl alcohol and syringaldehyde. On the other hand, β-oxysinapylalcohol as the major degradation product of acidolysis was not detected. This result suggested that the degradation mechanism of lignin by steam explosion is different from acidolysis. By the condition used. β-ether linkage of SS was cleaved homolytically and formed sinapyl alcohol radical. These adicals were homocoupled to give syringaresino1, and reduction of sinapyl alcohol radical formed sinapyl alcohol. The

results obtained from steam treated S-DHP and S-LCC were similar with that from SS. However, from steamed S-DHP, sinapaldehyde was obtained much more than that of sinapyl alcohol. The difference in the amounts of the degradation products possibly due to the different oxidation levels of the C6-C3 units of the molecule. ln the SS, each phenolic unit was subjected to one- electron oxidation (the oxidation level is similar to the sinapyl alcohol radical). In the S-DHP, to produce a polymer, one-electron oxidation occurred twice (the oxidation level is similar to sinapyl aldehyde radical). On the other hand, from steamed S-LCC, sinapyl alcohol was produced much higher than that of sinapaldehyde. Sinapyl alcohol radical results from the cleavage of β-ether by steam treatment was reduced by the hemicellulose exist in S-LCC.

1992-204

機能性リグノフェノール誘導体の調製およびその特性

松江淳介、船岡正光
三重大学農学部

Preparation of functional lignophenols and their characteristics

Junsuke Matsue, Masamitsu Funaoka
Faculty of Bioresources, Mie University

Abstract: A new conversion technique (SS Conversion Process) of protolignins and technical lignins into functional lignophenols has been developed. The characteristics of this process are as follows : 1. Rapid conversion at room temperature. 2. No special chemicals and equipment. 3. Selective phenolation at α-positions of lignin side chains. 4. Disappearance of conjugated systems. The resulting lignophenols have high reactivity and new functions as phenolic polymers. In the present paper, the characteristics and procedure of SS conversion process are described, compared with conventional phenolation techniques.

1992-205

高度の縮合構造を有する酸リグニンの可溶性リグノスルホン酸への変換

松下泰幸、安田征市
名古屋大学農学部

Conversion of highly condensed acid lignin into water-soluble lignosulfonate

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Faculty of Agriculture, Nagoya University

Abstract: Conversion of highly condensed sulfuric acid lignin into water-soluble lignosulfonate was investigated. At first, sulfuric acid lignin was phenolized to enhence its reactivity. Two methods were tried to convert phenolized SAL into water-soluble lignosulfonate. One was hydroxymethylation, followed by neutral sulfite treatment, and the other was sulfomethylation with hydroxymethane sulfonate. Sulfur content introduced by the two-step procedure was higher than that by the one- step method and commercial lignosulfonates. The two-step method gave higher molecular weight products than the one-step procedure, maybe because of polymerization during hydroxymethylation and sulfonation.

1992-206

カルボキシルメチル化リグニンの合成とその特性について

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Synthesis and properties of carboxymethylated lignin

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Abstract: The purpose of this study is to synthesize a water-soluble dispersing agent from water-insoluble lignin which is obtained from softwood by acetic acid-digestion. The dispersing agent was synthesized by carboxymethylation of the lignin with monochloroacetic acid. This carboxymethylation was successfully performed by heterogeneous reaction of the lignin dipped into 48% NaOH-aq. and monochloroacetic acid in 2-propanol (IPA). We found this carboxymethylated lignin was easily soluble in water and had a calcium sequestering capacity of 130mg-CaCO3/g and a dispersing power for Fe2O3 particles.

Keywords: 酢酸蒸解・リグニン・脱アセチル化リグニン・カルボキシメチル化リグニン・Caイオン捕捉能・分散能、dispersing agent, acetic acid cooking, deacetylated lignin, carboxymethylated lignin, calcium ion sequestering capacity, dispersibility

1992-207
リグニンを原料とするポリエステルポリウレタンの調製と熱的性質
広瀬重雄[*1]、小橋川健[*2]、畠山兵衛[*1]
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Preparation and thermal properties of polyester-polyurethanes derived from lignin
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Abstract: Polyurethane foams (PU) could successfully be prepared by the following procedure. A mixture consisting of a ethylene glycol (EG) solution of kraft lignin and polyester-polyol (PES, diol- type polycaprolactone, molecular weight 550) was reacted with diphenylmethane diisocyanate (MDl) in the presence of a small amount of water, tin catalyst and silicone surfactant. Thermal properties of PU's were studied by thermogravimetry (TG) and differential scanning calorimetry (DSC). Mechanical properties of the obtained foams were also studied by compression test. The effect of the addition of kraft lignin to PU's is considered in this paper.

1992-208
Synthesis and thermal properties of liquid crystalline aromatic copolyesters from phenols related to lignin
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Abstract: New aromatic copolyterephtahalates combining two hydroquinones such as: methoxy-hydroquinone (MHQ), 2,6-dimethoxyhydroquinone (DHQ) and 4,4’-dihydroxy-3,3’,5,5'- tetramethoxy-biphenyl (THQ), have been synthesized and characterized starting with lignin-related phenols. These copolymers showed liquid crystalline properties according to the observation by polarizing microscopy and differential scanning calorimetry.

1992-209
中温硬化型リグニン樹脂接着剤の製造
島谷啓二、佐野嘉拓
北海道大学農学部
Preparation of medium-temperature setting lignin-based wood adhesives
Keiji Shimatani, Yoshihiro Sano
Faculty of Agriculture, Hokkaido University

Abstract: The utilization of kraft lignin in the substrate of medium-temperature setting wood adhesives was investigated. A mixture of the lignin and phenol was hydroxymethylated under alkali conditions with various molar ratios of formaldehyde and methanol at 80 ºC for 2 hours. Resorcinol or wattle tannin and paraformaldehyde were added to the hydroxymethylated products in order to prepare the adhesives. The adhesives yielded high bonding strength and water resistance at hot pressing temperature of 100 ºC. The hydroxymethylated products were analyzed by GPC,^{1}H-NMR, ^{13}C-NHR, HPLC and so forth.

1992-210
酢酸リグニンの繊維化
久保智史[*1]、浦木康光[*1]、佐野嘉拓[*1]、笹谷宜志[*1]、小川正人[*2]
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Preparation of lignin fiber from acetic acid lignin
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Abstract: Acetic acid lignin (AWL) which was prepared from birch chips by atmospheric acetic acid pulping containing H2SO4 had a melt spinnability. However the lignin fiber spun out of AWL had a rough surface and had some micropores probably due to the elimination of low molecular weight volatile materials. In this study, we tried heat treatment of AWL as pretreatment to solve these problems. The heat treatment at l60 ºC reduced the amount of micropores of the surface. Consequently the treatment gave a easily spinning condition.

1992-211
硫酸触媒による常圧酢酸パルプ化 —単離リグニンの化学構造
堀崎敬史、島谷啓二、佐野嘉拓、笹谷宜志

北海道大学農学部
Pulping at atmospheric pressure with aqueous acetic acid containing a small amount of
sulfuric Acid. -Chemical structure of isolated lignins
Yoshifumi Horisaki, Keiji Shimatani, Yoshihiro Sano, Takashi Sasaya
Faculty of Agriculture, Hokkaido University

Abstract: Cellulose, hemicellulose, and lignin can be recovered quantitatively without tedious operation by atmospheric pulping with aqueous acetic acid containing a small amount of sulfuric acid. We reported that acetic acid lignins (AWL) with large amounts of phenolic hydroxyl groups had high reactivity, which may be useful for the substrate of synthetic phenol polymers. To examine the chemical structure of AWLs in detail, the content of phenolic and aliphatic hydroxyl, carbonyl and carboxyl groups, degree of condensation and so forth in AWLs were determined. And the effects of polysaccharides on delignification during pulping were also examined.

1992-212
The high efficiency of cellulose poduction by *Acetobacter xylinum* ATCC 10245 in a new culture medium with a sulfite pulping waste fraction
Siripong Premet、鮫島一彦、高村憲男
高知大学農学部
The high efficiency of cellulose poduction by *Acetobacter xylinum* ATCC 10245 in a new culture medium with a sulfite pulping waste fraction.
Siripong Premet, Kazuhiko Sameshima, Noiro Takamura
Faculty of Agriculture, Kochi University

Abstract: A new culture medium named KC medium (based on KOCHI) is a compound with a fraction of sulfite pulping waste (commercially available), glucose, yeast extract, peptone and buffer compounds. This nutrient culture medium showed high efficiency for cellulose production than the standard culture medium. *Acetobacter xylinum* ATCC 10245 was cultured in KC medium at static condition, and 2% glucose KC medium gave high cellulose membrane yield (about 300%) than 2% glucose standard medium.

1992-213
クラフトパルプ残留リグニンの特性 —S-S プロセスによる評価
浜口佳織、船岡正光
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Characterization of kraft pulp residual lignin by swelling-solvation process
Kaori Hamaguchi, Masamitsu Funaoka
Facult.y of Bioresources, Mie University

Abstract: Swelling-solvation (SS) technique was applied to separate and characterize kraft pulp residual lignins. The SS process has originally been developed for the quantitative separation of lignin with selective structural modifications from lignocellulosics. The key point of this process is to destroy carbohydrates by concentrated sulfuric acid under the solvation of lignin with cresol. The mass balance of residtlal ligrlins in the SS reaction system was determined in detail, and properties of SS separated residual lignins were compared with those of dissolved lignins subjected to the same SS treatment. Through these data, the chemical and polymeric characteristics of pulp residual lignins were discussed.

1992-214
リグニンの酵素分解に関する研究（III）メンブランフィルターを用いた培養系におけるクラフトパルプ残留リグニンの挙動
蔵敷賢二、近藤隆一郎、坂井克己
九州大学農学部
Modification of residual lignin in unbleached kraft pulp by extracellular enzymes excreted from white-rot fungi in a cultivation system using a membrane filter
Kenji Kurashiki, Ryuichiro Kondo, Kokki Sakai
Faculty of Agriculture, Kyushu University

Abstract: In a previous work, we demonstrated the modification of dioxane lignin by extracellular enzymes excreted from white-rot fungi using two membrane filters of different thickness, and suggested that the degradation of the low-molecular-weight dioxane lignin depended on the distance between the hyphae and the

lignin sample. In the present experiment, some beech unbleached kraft pulp sheets were treated in this cultivation system. About 10% of residual lignin in kraft pulp was degraded by treatment with *Phanerochaete chrysosporium* or *Coriolus versocolor* if the thin membrane filter was used, although almostt 100% of lignin was recovered in the thick-membrane system. The ligninolitic activities of fungus YK-624, and YK-472 which were isolated from decayed wood were superior to those of *P. chrysosporium* and *C. versocolor* in the thin-membrane system. Consequently, it was suggested that the degradation of the residual lignin in kraft pulp also depended on the distance between the hyphae and the surface of kraft pulp sheet.

1992-215

リグニン分解菌によるクラフトパルプ漂白廃液の処理（IV）自然界より分離したリグニン分解菌によるクラフトパルプ漂白廃液の脱色

李　宣鎬、近藤隆一郎、坂井克己
九州大学農学部

Decolorization of kaft bleaching effluent by lignin-degrading fungi (IV), Screening of wood-rotting fungi for efficierlt decolorization of kraft bleaching effluent

Seon-Ho Lee, Ryuichiro Kondo, Kokki Sakai
Faculty of Agriculture, Kyushu University

Abstract: To find a more efficient system for the decolorization of kraft pulp bleaching (E1) effluent, we have performed screening for high-decolorization fungi from l52 strains of isolated wood-rotting fungi. We observed that most of the guaiacol-colorization positive fungi showed the efficient decolorization of the E1 effluent. A highly significant correlation between the decolorization of the E1 effluent and the degradation of lignin in wood was not observed for isolated wood-rotting fungi. From decay wood samples we could isolate three fungi (MZ-227, MZ-400 and YK-624) having high decolorization activity of the E1 effluent with additional nutrients. Moreover, the fungus KS-62 showed the excellence in the decolorization and the reduction of the UV absorbance (280 nm) of the E1 effluent without any additional nutrients.

1992-216

酸処理によるクラフトパルプの無塩素漂白

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森林総合研究所

Acid treatment as one stage of non-chlorine bleaching

Shuji Hosoya, Yoichi Tomimura, Kinji Shimada
Forestry and Forest Products Research Institute

Abstract: Beech kraft pulp of a kappa number 20.5 was successfully delignified by 95 % acetic acid treatment with a small amount of hydrochloric acid at a refluxing temperature. The degree of delignification and the decrease in pulp viscosity highly depended on the amounts of hydrochloric acid added. The delignification was accelerated by the addition of nitrates and the selectivity increased. Finally the kappa number below five was achieved with the viscosity above twenty c.p.. Better result was also obtained in aqueous soluti , without using acetic acid, by adjusting the pH with sulfuric acid and applying the alkaline extraction after acid treatment.

1992-217

クラフトパルプの無塩素漂白.　オゾン漂白におけるパルプ粘度低下の機構

岸本崇生、中坪文明、村上浩二
京都大学農学部

Non-chlorine bleaching of kraft pulps, -Mechanism of viscosity drop in ozone bleaching

Takao Kishimoto, Fumiaki Nakatsubo, Koji Murakami
Faculty of Agriculture, Kyoto University

Abstract: A oxygen-bleached hardwood kraft pulp was treated with ozone at low consistency in acidic aqueous medium with sulfuric or oxalic acid and in methanol. These reaction conditions have been found to inhibit carbohydrate degradation. Here, we considered that the viscosity drop may be caused by two reactions, direct glycosidic bond cleavage during ozone bleaching and indirect reaction caused by carbonyl groups formed by oxidation. As a result of these experiments, it is indicated that methanol inhibits the direct glycosidic bond cleavage, not oxidation, contrary to the expectation reported earlier.

1992-218

漂白過程で生じる有機塩素化合物の性状

新谷博幸、松本雄二、飯塚堯介、石津　敦
東京大学農学部

Nature of chlorinated organic compounds

Hiroyuki Shintani, Yuji Matsumoto, Gyosuke Meshitsuka and Atsushi Ishizu
Faculty of Agriculture, the University of Tokyo,

Abstract: Unbleached hardwood kraft pulp, oxygen semibleached hardwood kraft pulp and unbleached softwood MCC pulp were chlorinated at various levels of chlorine ratio (0.1-0.3). The most significant difference between chlorinated lignin from softwood and that from hardwood is water solubility. Chlorolignin formed from hardwood kraft pulp is highly water soluble and, thus, considerable part of TOC (total organic carbon) and TOCl (total organic chlorine) are found in chlorination liquor, whereas only small part of chlorolignin became water soluble during chlorination of softwood pulp. Chemical structure of chlorolignin in oxygen semibleached pulp was quite different from that in non-semibleached pulp, and the former lignin was dissolved out more easily than the latter.

1992-219

リグニンペルオキシダーゼによるクロロフェノールの分解

藤井里絵、小野克正、松本雄二、石津　敦、桃原郁夫
東京大学農学部、森林総合研究所

Inhibition of lignin peroxidase oxidation of veratryl alcohol by chlorophenols

Rie Fujii, Katsumasa Ono, Ikuo Monohara, Yuji Matsumoto, Atsushi lshizu
Faculty of Agriculuture. the University of Tokyo

Abstract: When veratryl alcohol (VA) is treated with lignin peroxidase (Lip) in the presence of chlorophenols, the VA-oxidation is inhibited in a special manner. The inhibition period, which is difined as the time until VA-oxidation started, was analyzed in terms of concentrations of VA and chlorophenols. In the presence of an enough amount of VA, the inhibition period was proportional to the concentration of chlorophenols. With the increase in the concentration of VA, the inhibition period decreased and reached a minimum value. Kinetic analyses of this reaction indicated the presence of highly reactive species which are capable of degrading chlorophenols.

1992-220

クラフトパルプ前処理酸素漂白法の機構と新しい前処理方法の検索

大井　洋、田尻政直、岩永雄三、青柳哲夫、大内基弘
日本紙パルプ研研究所

Mechanism of pretreatment for oxygen bleaching of kraft pulp and a new pretreatment

Hiroshi Ohi, Masanao Tajiri, Yuzo lwanaga, Tetsuo Aoyagi, Motohiro Ohuchi
Japan Pulp a Paper Research Institute

Abstract: A new pretreatment method with nitrite, acid and oxygen for oxygen bleaching was proposed while mechanism of various pretreatments was discussed in this study. Although the pretreatment called Samuelson's S3 process fairly improves oxygen bleaching, it requires the two-stages pretreatment. Furthermore, in its first stage, the reaction is done with gas-phase nitrogen dioxide and a pulp of high consistency. These defects were removed for the new pretreatment method. For the improvement of oxygen bleaching, nitrite has an important role both in the second stage of S3 process and the new method. In the new method, oxygen should have an important effect on the oxidation of lignin and its activation for oxygen bleaching.

1992-特別講演 S-1

森林環境と微生物　—森林ときのこの共生

小川　真
株式会社、関西総合環境センター・生物環境研究所

Forest environment and microorganisms. Symbiosis between forest tree and mushroom

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The General Environmental Technos Co. Ltd.

Keywords: evolution, wood rotting fungi, mycorrhiza, vesicular-arbuscular mycorrhiza,

1992-特別講演 S-2

セルロース系材料の機能変換

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宮本武明

Functionality conversion of cellulosic materials by chemical modifications and structural controls

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Abstract: Recently cellulose has been reevaluated as a functional material to meet diverse needs of today's society. This is mainly due to the unique reactivities and molecular characteristics of cellulose, which is nontoxic, biodegradable, biocompatible, hydrophilic, chiral, and semi-rigid. Rather simple chemical modifications allow the conversion of cellulose to materials of novel functions for practical use, while conserving the cellulose characteristics mentioned above. Currently in the author's laboratory, by means of chemical modifications and structural controls, naturally occurring polymers like cellulose and chitin are attempted to be converted from mere structural polymers to new materials with special functions. This presentation intends to illustrate examples of cellulose modifications as broadly as possible. The topics include (i) substituents distribution control of conventional cellulose derivatives, (ii) thermoplasticization of cellulose and its applications, (iii) thermotropic liquid crystals and LB films from cellulose, (iv) highly dielectric cellulose derivatives, and (v) preparation and functionalization of oligosaccharides.

第38回（1993.11.15-16）四国電力株式会社 総合研究所

1993-101
熱分解ガスクロマトグラフィーによる広葉樹型リグニンの分析（I）アルカリ性ニトロベンゼン酸化との比較
和泉明子、黒田健一、山口　彰
筑波大学農林工学系
Analysis of hardwood lignin by pyrolysis-gas chromatography. I. Comparison of pyrolysis with alkaline nitrobenzene oxidation using synthetic lignin
Akiko Izumi, Kenichi Kuroda, Akira Yamaguchi
Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: Several synthetic lignins (DHPs) with various syringyl/guaiacyl ratios were prepared by the dialysis method, and Curie-point pyrolyzed at 500ºC for 4 s. The products were identified by GC/MS and estimated by GC with FID. The observed pyrolysis products were same as those from tochinoki (*Aesculus turbinata*). Yields of degradation products and their S/V ratios were compared with those by alkaline nitrobenzene oxidation.

1993-102
熱分解ガスクロマトグラフィーによる日本産針葉樹の分析
黒田健一、山口　彰
筑波大学農林工学系
Analysis of some Japanese softwoods by pyrolysis-gas chromatography
Kenichi Kuroda, Akira Yamaguchi
Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: To find out any difference in lignins between softwood species, an analytical pyrolysis technique, pyrolysis combined with gas chromatography (Py-GC), was applied to 16 Japanese softwoods. Twenty-five peaks of lignin-derived monomer pyrolysis products, 21 guaiacyl and 4 p-hydroxyphenyl type products, were displayed on all Py-GC traces of the softwoods pyrolyzed at 500 ºC for 4 s: no remarkable qualitative differences, hence, were observed. However, the Py-GC traces differed quantitatively. Distribution of *trans*-coniferyl alcohol in the lignin-derived products indicated that the pyrograms of Japanese softwoods examined are grouped into three types: the alcohol distribution in the selected lignin-derived products is (a) more than 20%, (b) around 15% and (c) less than 10%.

1993-103
ユーカリ属の組織化学的方法によるリグニンの分析（I）
渡辺陽子[*1]、深沢和三[*1]、船田　良[*1]、浅田隆之[*2]、小名俊博[*2]
[*1] 北海道大学農学部、[*2] 王子製紙株式会社林木育種研究所
Lignin analysis of Eucalyptus by histochemical methods (I)
Yoko Watanabe[*1], Kazumi Fukazawa[*1], Ryo Funada[*1], Takayuki Asada[*2], Toshihiro Ona[*2]
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Abstract: Lignin heterogeneity of Eucalyptus was investigated by using histochemical methods (Mäule reaction and ultraviolet microscopy). Absorption spectra of Mäule reaction showed that all samples were syringyl lignin rich type in all elements.

1993-104
樹木クラウンゴール細胞壁の化学構造と組織構造に関する研究
枝重有祐、富村洋一、藤井智之、石井　忠
森林総合研究所
Structural analysis of crown gall cell wall of *Populus kitakamiensis*
Yusuke Edashige, Yoichi Tomimura, Tomoyuki Fujii, Tadashi lshii
Forestry and Forest Products Research Institute

Abstract: Cell wall material was isolated from crown gall tumor and sound part of *Populus kitakamiensis*. Crown gall cll wall contained larger amount of lignin than the sound wd and the lignin was rich in condensed type. There was little difference in cell wall polysaccharides between them. The main hemicellulosic polysaccharide was 4-*O*-methylglucuronoxylan, which is a typical hemicellulose of hardwood. Callose, which is induced in infected cells, was not detected in the crown gall cell wall. Microscopic observation indicated that crown gall was consisted of normal cells, but that rapid cell division induced by *Agrobacterium tumefacience* made cambium abnormal form.

1993-105

リグニン化学構造の不均一性に関する研究　—β-O-4 構造の *erythro, threo* 比のリグニン存在部位による相違

松本雄二、南　一守、飯塚堯介、石津　敦

東京大学農学部

Structural heterogeneity of lignin, The ratio of erythro and threo type of arylglycerol-β-aryl ether structure in different part of cell wall

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Abstract: Ozonation method was applied to investigate how *erythro* and *threo* ratio of arylglycerol-β-aryl ether structure (E/T ratio) is regulated. E/T ratio in a DHP synthesized by the stepwise addition method (Zutropfverfahren) was 3 : 1, whereas that in a DHP synthesized by the one time addition method (Zuraufverfahren) was about 1 : 1. E/T ratio in MWLs extracted from stepwisely milled wood meal increased with the increase in milling time, indicating that E/T ratio in secondary wall lignin is higher than that in compound middle lamella lignin. On the basis of these results, we concluded that in a endwisely polymerized lignin (secondary wall lignin), *erythro* type of arylglycerol-β-aryl ether structure is preferentially formed, and that in a bulk polymer type lignin (compound middle lamella lignin) *threo* type becomes relatively important.

1993-106

デヒドロジコニフェリルアルコールの光学分割と絶対配置の決定

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Optical resolution and absolute configuration of dehydrodiconiferyl alcohol

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Abstract: The absolute configuration of dehydrodiconiferyl alcohol was elucidated by a chemical degradation. (+)-Dehydrodiconiferyl alcohol was prepared by optical resolution of the racemate with HPLC. The value of specific rotation was +63.3° , suggesting that the natural (+)-dehydrodiconiferyl alcohol isolated from milk thistle ([a]D +10.9°) was not optically pure. (+)-Dehydrodiconiferyl alcohol was degradated to methylsuccinic acid via several steps. The methylsuccinic acid was (R)-(+)- enantiomer, the optical purity of which was confirmed by HPLC after derivatization. This showed that the absolute configuration of C-2 of (+)-dehydrodiconiferyl alcohol was S. Since H-2 and H-3 of dehydrodiconiferyl alcohol is trams, the absolute configuration of C-3 is inevitably R. Thus (+)-dehydrodiconiferyl alcohol is 2S and 3R.

1993-107

リグニン、フミン酸の酸化還元的性質　—ESR による解析

鬼木隆幸

九州歯科大学

Redox properties of humic acid and lignin, -Electron spin resonance study

Takayuki Oniki

Kyushu Dental College

Abstract: Electron spin resonance (ESR) spectra of humic acids and lignin were measured at pH 13.0 under argon atmosphere or after air bubbling with or without redox reagents. ESR signal intensities of humic acids increased with elapsed time, whereas those of lignins decreased. The signals of humic acids dccreascd by oxidation with O2 or K3[Fe(CN)6] but original signals were recovered as time elapsed. The signal of lignins increased by the oxidation. The intensities of humic acids increased by reducuon with a small amount of Na2S2O4 but decreased with a large amount of Na2S2O4. The intensities of lignins decreased with a small amount of Na2S2O4. Lignins were found to be a more reduced state than humic acids.

1993-108

コブシ細胞壁形成過程におけるモノリグノールグルコシドの挙動

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Behavior of monolignol glucosides during cell wall formation of magnolia

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Abstract: To examine the behavior of glucose residue of monolignol glucosides jn cell wall lignification, coniferin-[Glc-6-^{3}H, β-^{14}C] was administered to magnolia two-years old shoot. After 3 hours or 7 days feeding, coniferin and syringin were isolated from the sap and each radioactivity was measured. The ^{3}H-activity was observed not only in coniferin, but in syringin. It suggests the introduction of methoxyl group may occur in the state of monolignol glucosides. The decrease of ^{3}H (glucose) to ^{14}C (lignols) in monolignol glucosides was little at the end of 3 hours feeding, and increased corresponding to the length of feeding period. The ratio of ^{3}H-decrease of monolignol glucosides in phloem region was larger than that in newly formed xylem region.

1993-109

Expression of brown midrib mutations on grass lignin

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Abstract: Studies were conducted to characterize cell wall phenolic composition in diverse genotypes of grasses, including bmr6 and bmr12 sorghum lines, and bm1, bm2, bm3 maize lines and their normal counterparts. All brown midrib genotypes contained lower lignin content and alkali-labile p-coumaric acid. The monomer composition of lignin was differently altered according to the bm(r) gene. The occurrence of 5-hydroxyguaiacyl was shown in the alkyl aryl ether structures of bmr12 lignin of sorghum as previously reported for bm3 maize mutants. In these plants, the non-condensed lignin structures incorporated a low proportion of syringyl unit in contrast to the maize bm2 lignin which contained less guaiacyl moieties than normal lignin. Furthermore, bmr6 sorghum incorporated cinnamaldehydes units in the lignin polymer. The variations in the relative proportions of guaiacyl and syringyl units indicated that the bm(r) mutations cause different lignin structural changes. Therefore, the phenotypically similar brown midrib plants originate from different modifications of the lignification pathway.

1993-110

ウド CAD アンチセンス遺伝子を導入したタバコの解析

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Anaysis of tobacco plants with an antisense cinnamyl alcohol dehydrogenase transgene from *Aralia cordata*

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Abstract: Cinnamyl alcohol dehydrogenase (CAD) catalyzes the reduction of hydroxycinnmic aldehydes (para-coumaryl, coniferyl, and sinapyl) to the corresponding alcohols (monolignols) in lignin biosynthesis. Thus, CAD is an important target in genetic engineering to modify lignin content or quality. We tested CAD activity in some tobacco plants carrying an antisense gene constructed with *Aralia cordata* CAD cDNA. CAD activity of one of transgenic tobacco plants was decreased about 55 % in comarison with that of a normal tobacco plant. Observation of cross-sections of shoots stained for lignin by the phloroglucinol-HCl assay provided evidence that more aldehydes accumlate in the cell wall in the transgenic tobacco plant than in normal tobacco plants.

1993-111

シュート分化により誘導される交雑ヤマナラシおよびタバコの酸性ペルオキシダーゼアイソザイムの発現解析

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Expression analysis of anionic peroxidases correlated with shoot forming in *Nicotiana tabacum* and *Populus kitakamiensis*

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We have analysed the expression of peroxidase isozymes correlated with shoot forming in *Nicotina tabacum* and *Populus kitakmniensis*. Several anionic isozymes were found to express in the callus forming vegetative bud or regenerating shoot but not in callus or leaf tissue. We have already isolated *N. tabacum* genomic peroxidase clones (*poxA1* and *poxC1*) and *P. kitakamiensis* genomic clone (prxA1). In this report, we have isolated two other novel peroxidase clones from *P. kitakamiensis* cDNA library. Using these peroxidase genes as probes, expression patterns of anionic peroxidases were examined by RNA blot analysis.

1993-112

樹木フェニルアラニンアンモニアリアーゼ遺伝子群の構造と発現の解析

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Characterization and expression of phenylalanne ammonia-lyase genes from a woody plant (*Populus kitakamiensis*)

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Abstract: Six independent phenylalanine ammonia-lyase (PAL) genes were isolated from a genomic library and a cDNA library constructed win mRNAs from the young stem tissue of a hybrid aspen, *Populus kitakamiensis*. The isolated PAL clones from the cDNA library were transcribed from one gene. The corresponding gene (*pal g1*) to the cDNA and four other genes were isolated from the genomic library. Most of PAL genes consist of two exons divided with one intron. Interestingly, *pal g2a* and *pal g2b* were isolated as one DNA fragment containing two tandemly oriented PAL genes. The expressions of these PAL genes in stem, leaf, and callus tissues were demonstrated by RNA blot analysis using gene-specific probes. lt was defined that *pal g1* was mainly transcribed in the young stem tissue.

1993-113

リグニン生合成系に関与するOMT酵素蛋白と遺伝子の単離

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Purification of *O*-methyltransferase (OMT) involved in the lignin biosynthesis and cDNA cloning

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Abstract: *O*-methyltransferase (OMT) is a key enzyme for deterninating aromatic ring structures in lignin. We obtained two OMT activities from a hybrid aspen, *Populus kitakamiensis,* by using anion exchange chromatography and affinity chromatography on *S*-adenosyl-L-homocystein- Sepharose 4B. The results of Southern hybridization for total DNA from *P. kitakamiensis* suggested that OMT was consisted of a snmall gene family. We isolated a DNA fragment encoding OMT from a cDNA library constructed with the stem RNA and it was very similar to OMT genes from aspen and poplar.

1993-114

Pseudomonas paucimobilis SYK−6 株のビフェニル環開裂酵素遺伝子の単離と解析

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Cloning and analysis of the genes of biphenyl ring fission from *Pseudomonas paucimobilis* SYK-6

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Abstract: *Pseudomonas paucimobilis* SYE-6 grows on various lignin dimeric compounds as a sole carbon souce. In particular, it is characteristic of this strain to degrade biphenyl compounds. We have already reported about the metabolism of biphenyl structure in lignin and cloning of 15-kbp EcoR I fragment which could restore the wild's phenotype of mutants. We explain that l5-kbp EcoR I fragment is related to degradation of biphenyl compounds.

1993-115

リグニンビフェニル型化合物の分解酵素遺伝子群の単離と解析（脱メチル酵素遺伝子の単離と解析）

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Cloning and analysis of the genes involved in degradation of biphenyl structure of lignin compounds Cloning and analysis of the demethylase gene.

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Abstract: *Pseudomonas paucimobilis* SYK-6 is able to grow on DDVA and other various lignin dimeric compounds as a sole carbon source. To reveal of the specific reactions of lignin metabolism of microorganism, we investigate the metabolism of biphenyl compound DDVA by SKY-6. We have isolated the gene coding DDVA demethylase as a 30kb *Sal* I DNA fragment (plasmid clone pDM22) from *Pseudomonas paucimobilis* SYK-6 chromosomal DNA. Here, we have isolated another clone which has a 6kb EcoR I fragment (plasmid clone pLE6), which is thought to be the same of the 6kb EcoR I fragment in pDM22.

1993-116

リグニンペルオキシダーゼによるチトクロ−ム C の酸化

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Oxidation of ferrocytochrome c by lignin peroxidase

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Abstract: The direct oxidation of ferrocytochrome c by lignin peroxidase (LiP) from the lignin degrading basidiomycete, *Phanerochaete chrysosporium*, was demonstrated. As with cytochrome c peroxidase reactions, LiP oxidation of ferrocytochrome c decreased as the ionic strength increased, implying the involvement of electrostatic interactions between the polymeric substrate and enzyme. The reaction product ferricytochrome c inhibited veratryl alcohol oxidation by LiP in a noncompetitive manner, suggesting that cytochrome c binds to LiP at a site different from the small aromatic substrate binding site. Recent crystallographic studies show that the heme is buried in the LiP protein and unavailable for direct interaction with polymeric substrates, suggesting that the electron transfer from ferrocytochrome c to LiP may occur via electron tunneling, as in the reaction of cytochrome c peroxidase with ferrocytochrome c. This observation of the direct oxidation of ferrocytochrome c by LiP may serve as a useful model for probing the mechanism of electron transfer between the buried heme of the enzyme and polymeric substrates.

1993-117

有機溶媒中における化学修飾ペルオキシダーゼの反応

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Reaction of chemically modified peroxidase in organic solvents

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Abstract: Lignin peroxidase (LiP) from *Phanerochaete chrysosporium* was chemically modified with methoxypolyethylene glycol-succinimidyl succinate (MPSS). Reaction products by the native and modified LiP in organic solvents were analyzed by g.1.c. 3,4,5-Trimethoxybenzyl alcohol (TMBA) was oxidized by the modified LiP in benzene, While the native LiP was inactive to TMBA in the organic solvent. Furthermore, it has been found that veratryl alcohol was more susceptible to the oxidation than TMBA in aqueous solutions, while the reverse substrate specificity was observed in the reactions in benzene. Oxidation activity of the modified LiP in benzene was 1/300 of that observed in aqueous solution.

1993-118

Phanerochaete chrysosporium の芳香環開裂酵素について（II）

中村雅哉、西田篤実、高野麻理子
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Aromatic ring cleavage enzyne from *Phanerochaete chrysosporium* (II)

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Forestry and Forest Products Research Institute

Abstract: In the metabolic pathway for vanillic acid degradation by *Phanerochaete chrysosporium*, it was shown that 1,2,4-tri-hydroxybenzen underwent aromatic ring-cleavage. However, ring-fission dioxygenase is very unstable so the purification of this enzyme is very difficult. In this study, we succeeded in the purification of 1,2,4-trihydroxybenzen (hydroxyquinol) 1,2-dioxygenase and clarified some enzymatic properties. The native molecular weight of this enzyme is 94,000 Dalton and subunit molecular weight are 40,000 and 52,000 Dalton by SDS-PAGE. In the kinetic analysis, Michaelis constant for 1.2.4-tri-hydroxybenzen equals 7μM and Vmax equals 0.826.

1993-119

リグノスチルベン-α,β-ジオキシゲナーゼの活性と鉄の関係（II）

鴨田重裕、佐分義正
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The relation between activity and iron content of lignostilbene-α,β-dioxygenase (II)

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Abstract: Lignostilbene-α,β-dioxygenase I (LSD-I), one of LSD isozymes, contained iron. Native LSD-I was almost colorless or pale yellow at high concentration. LSD-I did not show the heme typical absorption spectrum. LSD-I seemed to have nonheme iron. LSD-I was inactivated by H2O2, oxidizing agent, and was activated by hydroxylamine, reducing agent, o-phenanthroline, chelating agent for ferrous ion, inhibited the LSD reaction. Tiron, chelating agent for ferric ion, did not inhibit the LSD reaction. LSD-I inactivated by H2O2 was reactivated with ferrous ion and hydroxylamine. These results indicated that ferrous ion play the important role on the enzyme activity. Furthermore, linear relation was founded between the amounts of ferrous ion and activities. The maximum amount of iron seemed to be two atoms per one molecule of LSD-I.

1993-特別講演、

植物培養細胞の二次代謝機能 —シキミ酸経路由来の shikonin と berberine を例に

福井宏至
香川大学農学部

Invited Lecture: Secondary metabolism (shikonin and berberine) in cultured plant cells

Hiroshi Fukui
Faculty of Agriculture, Kagawa University

1993-201

リグニンからのポリウレタン

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[*1] 森林総合研究所、[*2] 群馬女子短期大学

Polyurethanes from lignin

Shojiro Hishiyama[*1], Seiji Ohara[*1], Yasunori Hatano[*1], Kenichi Sudo[*2]
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Abstract: In order to prepare the polyurethane from lignin, lignin derivatives (I and II) were synthesized from steam-exploded lignin using glycerol α-monochlorohydrin (GMH). NMR studies show that lignin derivative II possesses large amount of hydroxyl groups which have high reaction activity with isocyanate. Preparation of polyurethane films was accomplished from lignin derivative II using two kinds of isocyanate, hexamethylenediisocyanate (HDI) and diphenylmethanediisocyanate (MDI). Viscoelastic properties of these polyurethane films were investigated.

1993-202
リグニン樹脂接着剤の製造
島谷啓二、佐野嘉拓、笹谷宜志
北海道大学農学部
Preparation of lignin-based wood adhesives
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Abstract: The utilization of kraft lignin in the substrate of wood adhesives has been investigated. A mixture of kraft lignin and phenol (8:2) was hydroxymethylated under alkali conditions in order to produce phenol-lignin co-polymer (WI and WS). WI was recovered in a yield of 89% from the reaction mixture. Resorcinol terminated resins of the co-polymers (WI-R) were prepared by condensation of WI (100 parts) with resorcinol (ca 30 parts) in alkali solution at pH 11. An alkali solution of WI-R (40% solids) containing 5-10% of paraformaldehyde had a gelation time of 25 minutes at room temperature. The gelation times varied with amounts and kinds of cross-linking reagents suggesting that wood lignins may be utilized as a readily available and inexpensive substrate for cold-setting wood adhesives.

1993-203
膨潤—溶媒和プロセスによる高反応性リグニンの合成
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Synthesis of highlyy reactive lignins by the swelling-solvation process
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Abstract: The swelling-solvation process is a method for direct conversion of protolignin into functional lignophenol derivatives, which proceeds rapidly at room temperature. The key point of this process is to treat lignocellulosics with concentrated acid under the solvation of lignin with phenol derivatives. The resulting lignohenol derivatives have several distinctive properties which conventional lignins do not have: no conjugated system, light color, high protein adsorbing capacity, etc. ln this presentation, the processes for synthesizing lignophenol derivatives having different reactivities and functions are discussed.

1993-204
隣接基関与反応を応用するリグノフェノール誘導体の分子構造変換
寶勝智貴、船岡正光、阿部　勲
三重大学生物資源学部
Structural conversion of lignophenol derivatives by neighbouring group participation
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Faculty of Bioresources, Mie tJniversity

Abstract: Lignophenol derivatives are directly derived from protolignin by the swelling-solvation process combining the solvation of lignin with phenol derivative and the swelling and dissolution of carbohydrates by concentrated acid. Lignophenol derivatives are not subjected to complicated structural modifications, retaining structural characteristics of original lignin, and highly phenolic, due to the cleavage of benzyl ether linkages and the phenolation at α-positions (0.65mol/C9 in softwood, 0.90mol/C9 in hardwood). In the present work, the lignocresols were synthesized from spruce and birch by the S-S process, and their depolymerizations were carried out by the neighbouring group participation in alkaline systems, in order to corltrol their reactivities and functions. Spruce lignocresol was depolymerized to Mw ca. 900 by the treatments with 2N NaOH or a mixture of NaOH and Na2S at l70 ºC for 2 hours, while birch lignocresol to Mw ca. 600. When *p*-cresol was added in the reaction system, spruce lignocresol decreased toMw ca. 600. Alkaline depolymerization mechanisms of lignophenol derivatives were discussed.

1993-205
リグノフェノール誘導体の構造とタンパク質に対するその機能
井岡浩之、関　範雄、中嶋礼子、三亀啓吾、○船岡正光、阿部　勲
三重大学生物資源学部
Affinity of lignophenol derivatives for proteins

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Faculty of Bioresources, Mie University

Abstract: Lignophenol derivatives were synthesized from various lignocellulosics, using the swelling-solvation process, and their affinity for proteins was investigated. Lignophenol derivatives had much higher affinity for proteins, compared with conventional lignin preparations. The protein adsorbing capacities of lignophenol derivatives differed with their originating species and increased with increasing basicity of phenol derivatives. The adsorption of protein on lignophenol derivatives rapidly took place at the initial step of treatment, after which the amount increased gradually with time. The maximum adsorption was achieved at isoelectric points of proteins. Proteins immobilized on lignophenol derivatives were not desorbed at any pH.

1993-206

リグニンの水素化分解 —触媒等の検討—

小山 実
物質工学工業技術研究所

Hydrocracking of lignin. -Search for catalysts and reaction conditions

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National Institute of Materials and Chemical Research

Abstract: Hydrocracking of a kraft lignin (KL) was conducted in order to search the catalysts and reaction conditions as the purpose to rise monophenol yield and promote the mononerization of KL. The searched catalysts were as follows; solid acids (smectites, aluminosilicates, Al-pillared smectites, composite metal oxides, zeolites and titanium oxides), alumina, metal oxides and metal.

1993-特別講演、

樹木抽出成分 —フェニルプロパン誘導体—

笹谷宜志
北海道大学農学部

Invited Lecture: Wood extractives, -Phenylpropane derivatives

Takashi Sasaya
Faculty of Agriculture, Hokkaido University

Abstract: In numerous wood extractives, typical phenylpropane derivatives are lignans. They include those based on the new definition, namely neolignans. This paper summarizes the chemical structures of lignans and neolignans in larch *Larix leptolepis* Gord., fir *Abies sachalinensis* Masters, willows *Chosenia arbutifolia* A. Skvortz. and *Salix sachalinensis* Fr. Schm. Among them, trimeric and tetrameric derivatives were involved in addition to dimeric ones. It is presumed that there is intimate relation between lignans and Brauns' lignin (BL). Also, the biological activities of lignans will be dealt with only briefly here.

1993-207

稲ワラ・ソーダ蒸解黒液リグニンの分散剤としての利用

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Utilization of rice straw soda lignin from pulping black liquor as dispersant

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Abstract: Soda lignin was isolated from the pulping black liquor of rice straw, then was sulfomethylated (SWL). The dispersibility of kaolin suspension and the setting of mortar with SWL were measured in contrast with wood lignosulfonate. The effects of dispersing additives were also tested with various carboxylic acids. The results are summarized as follows: (1) Dispersibility with rice straw SWL is efficient for concrete production. (2) Among the additives used here, sugar carboxylic acids are better than other carboxylic acid, and glucaric acid is superior than gluconic acid. (3) In order to simplify the sulfomethylation, lignin in black liquor was directly sulfomethylated after the acidification with dil. sulfurous acid. The dispersibility is poor comparing with that of purified SWL. The setting of mortar takes a long tine.

1993-208

リグニングラフトポリマーのセメント粒子への分散性と粘稠性

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The dispersibility and viscosity of lignin graft polymer to cement particles

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Keywords: lignin graft polymer, lignosulfonates, cement particles, dispersing agent, viscosity

Abstract: In this study, the synthesis of lignin graft polymer provides high-dispersibility and moderate viscosity for cement particles was investigated. Acrylamide (AM) and acrylamide methylpropansulfonate (AMPS) were grafted to lignin sulfonate (LSA) for which AM provides the viscosity and AMPS provides the high dispersibility. Various lignin graft polymers (LGP) were evaluated dispersibility and viscosity in cement mortar testings. It was found that LGP provided the high-dispersibility and the moderate viscosity to the cement particles.

1993-209

常圧酢酸パルプ化

金野晴男、佐野嘉拓、笹谷宜志
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Acetic acid pulping at atmospheric pressure

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Faculty of Agriculture, Hokkaido University

Abstract: Atmospheric pulping of commercial hardwood chips of Hokkaido in a boiling aqueous AcOH with a small amount of sulfuric acid were carried out either in a batch system or in a mimetic continuous-extraction system. The continuous extraction conditions used for the chips were the optimum conditions for separating into each of the main components as quantitatively as possible. By the continuous extraction in a boiling 95% AcOH with 0.32% sulfuric acid, the chips yielded 44.6% of screened pulp with Klason lignin of 6.9%, 1.8% of reject, 16.9% of reducing sugars (14.1% of xylose) and 19.0% of AcOH lignin based on o.d. chips, respectively.

1993-210

リグニンモデル化合物のオルガノソルブパルプ化処理における β-O-4 結合の開裂機構（II）—キノンメチド生成速度に対する有機溶媒の効果

高橋一郎、坂井克己
九州大学農学部

The β-O-4 bond cleavage mechanism during organosolv pulping treatments of lignin model compound, I. - The effect of organic solvent on rate of quinone methide formation-

Ichirou Takahashi, Kokki Sakai
Faculty of Agriculture, Kyushu University

Abstract: The β-O-4 bonds n lignin and its model compounds were cleaved to give eugenol and/or isoeugenol during an organosolv pulping treatment with bisulfite at 160 ºC. It was found that this reaction which proceeds *via* a quinone methide intermediate was seriously influenced by concentration and inductivity of organic solvents, Consequently we presumed that the rate- determining step is an ionic reaction. In order to investigate the effect of solvent on rate of quinone methide formation, a lignin model compound shown in Fig. 1 was subjected to an alcohol-phosphate buffer treatment in aqueous ethanol of various concentration at relatively low temperatures. The rate constants and activation parameters were calculated for *erythro* form to *threo* form. The conversion rate was affected seriously by solvent concentration. This result suggests that the rate-determining step of this reaction is not the β-O-4 bond cleavage process, but the quinone methide formation process.

1993-211

パルプ漂白菌によるリグニンモデル物質の変換

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Transformation of lignin model compounds by pulp-bleaching fungi

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Keywords: pulp-bleaching fungus, oxygen-bleached pulp, lignin degradation fungus, enzyme activity

Abstract: We have already reported a new pulp-bleaching fungus, namely SKB-1152, which could increase the brightness of oxygen-bleached kraft pulp (OKP) to over 80%. In the present work, we investigated the change of three lignin model compounds (veratryl alcohol: VE, veratric aldehyde : VEA, veratric acid : VEacid) when these compounds was added to the OKP in bleaching. After incubation, culture filtrate were analyzed by HPLC. VE was oxidized to VEA and VEA was consumed in the treatment by SKB-1152. However, when VEA and VEacid were added, these compounds were reduced to VE respectively. Resulting, produced VE was oxidized to VEA again and finally consumed. Further, we reported the enzyme activity in culture filtrate.

1993-212

機械パルプの微生物処理に関する研究（XI） 光退色を抑制する菌とモデル化合物との反応性について

谷口新吾、武田早苗、橘 燦郎、伊藤和貴、沖 妙
愛媛大学農学部

Studies on biological treatment of mechanical pulps (XI), Reactivity between lignin model compounds and extracellular crude enzymes solution from fungi having ability for depression of color reversion of mechanical pulps

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Abstract: Reactions between the lignin model compounds having functional groups for color reversion and the crude enzymes solution from six wood-rotting fungi having ability for depression of color reversion of mechanical pulps were examined. The model compounds used were coniferyl- aldehyde methy wther (1), α-(2-methoxyphenoxy)- β-hydroxypropioguaiacone (2), and methoxy-p- quinone (3). The compound (3) was most reactive to the crude enzymes solution in the three compounds, the compound (1) was next to the compound (3), and the compound (2) was less reactive. Main reaction of each compound was reductive reactions, but some oxidative reactions was also occurred. When the compound (3) was treated with the crude enzymes solution, main reaction was reduction of quinone to the corresponding hydroquinone and followed by methylation of the phenolic hydroxyl group generated. Based on the results of the reactivity between the model compounds and the crude enzymes solution, reduction of quinone and followed by protection of the phenolic hydroxyl group generated seem to contribute mainly to the depression of color reversion of mechanical pulps.

1993-213

リグニン分解菌によるクラフトパルプ漂白廃液の処理（VI）グルコノ-δ-ラクトン添加による処理性向上の機構について

李 宣鎬、近藤隆一郎、坂井克己
九州大学農学部

Decolorization of kraft bleaching effluent by lignin-degrading fungi (Vl), The mechanism of the decolorization of E1 effluent by an addition of glucono-δ-lactone

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Abstract: In a previous report, we observed that the addition of glucono-□-lactone to the E1 effluent showed great decolorization during a short treatment period. In the present study, we have attempted to clarify the mechanism of decolorization by the addition of glucono-δ-lactone. When the aqueous solutions of glucose and glucono-δ-lactone were treated with *Coriolus versicolor*, most of the glucose was consumed and the glucono-δ-lactone was converted a part into gluconic acid remaining in the cultivation medium. The pH of the effluent With the glucono-δ-lactone was decreased from an initial pH of 4.5 to 3.6, although the pH of the effluent without any additives was increased gradually during fungal treatment. From the results, we assume that the effect of the glucono-δ-lactone on the great decolorization of E1 effluent was due to the some morphological change of the mycelium of the *C. versicolor* by the gradual decrease of pH.

1993-214

白色腐朽菌のリグニン分解に関与する酵素系に関する研究（II）クラフトパルプのバイオブリーチングに及ぼす金属塩の影響

平井浩文、近藤隆一郎、坂井克己
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Studies on ligninolytic enzymes of white-rot fungi (II)
Effects of metal salts on biological bleaching of kraft pulp.

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Faculty of Agriculture, Kyushu University

Abstract: We obtained several new isolates which showed higher ligninolytic activity and selectivity than typical lignin-degrading fungi, *Phanerochaete chrysosporium* and *Coriolus versicolor*. In the present work, we applied these new isolates to bleaching of the kraft pulp, and determined ligninolytic enzyme activities in these bleaching cultures. Manganese peroxidase (MnP) was dominant in most strains which could bleach the kraft pulp, and the higher brightness increase of fungal treated pulp was observed, the higher MnP activity was detected in the culture. If metal ions were removed from the kraft pulp with an acid treatment, biological bleaching of the pulp hardly showed brightness increase, and ligninolytic enzyme activity in the culture sharply decreased. These results suggest that metal ions in the kraft pulp played an important role in biological bleaching of the kraft pulp by white-rot fungi.

1993-215

リグニンの酵素分解に関する研究（IV） メンブランフィルターを用いた培養系におけるクラフトパルプの *in vitro* ブリーチング

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In vitro bleaching of haft pulp by extracellular enzymes excreted from white-rot fungi in a cultivating system using a membrane filter

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Abstract: To clarify the role of the excreted extracellular enzymes during long-term incubation in biobleaching with white-rot fungi, we have developed a cultivation system using a membrane filter which can prevent the direct contact between hyphae and kraft pulp, but allows extracellular enzymes to attack the kraft pulp. The fungus YK-624 brightened the pulp 21.4 points to 54.0% brightness after 5-days *in vitro* treatment, which was significantly higher than *Phanerohaete chrysosporium* and *Coriolus versicolor* did during 7-days treatment. This results indicate that cell-free, membrane-filtered components from the *in vitro* biobleaching system are capable of delignifying unbleached kraft pulp. Obvious candidates for filterable reagents capable of delignifying and bleaching kraft pulp are peroxidase and phenoloxidase proteins. Secreted manganese peroxidase activity in the filterable components was substantial during the fungus YK-624 *in vitro* biobleaching. A positive correlation between the level of manganese peroxidase and brightening of the pulp was observed.

1993-216

亜硝酸前処理を用いるクラフトパルプ酸素漂白法とその漂白機構（2） アカマツパルプの亜硝酸処理とリグニンモデル化合物の反応

大井 洋、岸野正典、山口 彰
筑波大学農林工学系

A pretreatnent with nitrous acid for oxygen bleaching of kraft pulp and its bleaching mechanism (II), Nitrous acid treatment of akamatsu pulp and reactions of lignin model compounds

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Abstract: To clarify the conditions of nitrous acid pretreatment for softwoods pulp, akamatsu kraft pulp (kappa number: 26, viscosity: 3lcP) at medium consistency was treated under various conditions. Kappa number of the pulp decreased to 13.5 under the condition of 0.3% nitrite, 4% nitric acid, 90 ºC and 3 hours. Secondly we discussed about the bleaching mechanism based on reactions of non- phenolic lignin mdel compounds. When 1-(3,4-dimethoxyphenyl)-2-(2-methoxy-4-methylphenoxy)- propan-1-ol was treated in the nitric acid solution without nitrite at 90 ºC, it was stable even after 3 hours, which changed into an its stereo chemical isomer. More than 90% of the model was recovered. On the other hands, the model was clearly decomposed when it was treated with the nitrite and nitric acid, we identified 35% of veratraldehyde and 6% of 4-nitroveratrole from the model. It was found that a main reaction is the cleavage of a Cα-Cβbond.

1993-217

酸処理を用いたクラフトパルプの無塩素漂白 ―漂白機構―

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Non-chlorine bleaching by acid rreatment of kraft pulp, -Bleaching mechanism-
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[*1]Institute of Agricultural and Forest Engineering, University of Tsukuba, [*2]Forestry and Forest Products Research Institute

Abstract: It was reported in our previous paper that beech and red pine kraft pulp were successfully delignified by sulfuric acid treatment. with a small amount of sodium nitrate and sodium nitrite followed by caustic extraction. In this paper, the structure of the lignin dissolved by acid treatment or caustic extraction were characterized by elemental analysis UV, IR, NMR, and GPC to understand the delignification mechanism. Carbohydrate analysis of the pulp and the bleach effluent were also performed by using liquid chromatography to see the degradation of cellulose and hemicellulose during bleaching.

1993-218
酸素アルカリ漂白過程における多糖類の分解機構(2)—糖分解がリグニン反応に依存する系での反応選択性の向上—
安本光夫、松本雄二、石津　敦
東京大学農学部
Dependence of carbohydrate degradation on reaction of lignin during oxygen bleaching
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Faculty of Agriculture, the University of Tokyo

Abstract: During oxygen bleaching, the degradation of carbohydrate depends on the reaction of lignin. Therefore, mechanistic studies such as degradation pathway of carbohydrates, factors affecting reaction selectivity, or protective effect of additives have to be performed in a system where carbohydrate degradation is hardly observed if lignin is absent. In our model system, methyl- β-glucopyranoside (MGP) is not degraded when either vanillyl alcohol (VA) or oxygen is not present. Effects of oxygen pressure, magnesium to iron ratio, and methanol addition on the reaction rate of both MGP and VA, and on the reaction selectivity between MGP and VA were examined in this model system. Results suggested that degradation products of lignin peroxides rather than hydrogenperoxide or superoxide anion have a significant effect on the degradation of carbohydrate.

1993-219
The Contribution of high molecular lignosulfonate to the powerful bacterial cellulose production by *Acetobacter xylinum* ATCC 10245
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高知大学農学部

Abstract: The high molecular lignosulfonate fraction and the low molecular lignosulfonate and carbohydrate mixture fraction were obtained through gel-filtration and a 80% ethanol precipitation method from the commercial sulfite pulping waste fraction (named CP powder). The media with high molecular lignosulfonate fraction showed better yields than those with the low molecular carbohydrate rich fractions. The elimination of carbohydrates, cations and low molecular fraction from the whole CP powder showed no negative effect on the powerful cellulose production. The powerful cellulose production was also observed by the addition of commercially pure sodium lignosulfonate. The contribution of the dispersing nature of the lignosulfonate was compared with synthetic dispersant and natural digitonin but they showed only slight effects on cellulose production.

1993-220
微粉砕セルロースの生成に及ぼす因子
遠藤貴士、北川良一、細川　純、壁谷　洋、西山昌史
四国工業試験所
Factors for production of fine-grinding cellulose
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Government Industrial Research Institute, Shikoku

Abstract: Air-dried or vacuum-dried CF11 (Whatman) was ground in a vibratory ball mill under several conditions, and then the obtained powders were characterized. In case of both air-dried and vacuum-dried CF11 at room temperature, the particle size of powders became small and the crystallinity was decreased with grinding time. However, the degree of polymerization was not significantly reduced. In vacuum-dried CF11, the particle size was much smaller than in air-dried one. The particle distribution was same in both air-dried and vacuum-dried CF11 grinding at -100 ºC, and the particle size of obtained powders was small. However, the crystallinity from air-dried CF11 was slightly decreased. Addition of organic solvents such as acetone on CF11 was effective in forming fine particles. In particular, fine particles were formed from dried CF11. For fine-grinding of cellulose, the absorbed water significantly effects on the production of powder. The absorbed water causes agglomeration of the particles and plasticizing of cellulose.

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1994-101

熱分解ガスクロマトグラフィーによる広葉樹型リグニンの分析（II） 日本産広葉樹の分析

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Analysis of hardwood lignin by pyrolysis-gas chromatography (II), Analysis of Japanese hardwoods

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Abstract: Several Japanese hardwoods were analyzed by pyrolysis combined with gas chromatography (Py-GC). The yields of pyrolysis products were about half of those on nitrobenzene oxidation. The ratios of syringyl-derived pyrolysis products to guaiacyl-derived pyrolysis products were in agreement with the ratios of the syringaldehyde yields to the vanillin yields on nitrobenzene oxidation.

1994-102

熱分解ガスクロマトグラフィーによるイネ中の桂皮酸類の分析

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Analysis of cinnamic acids in rice (*Oryza sativa* L.) by pyrolysis-gas chromatography

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Abstract: Pyrolysis derivatisation using tetramethylammonium hydroxide (TMAH), a thermally assisted hydrolysis and methylation method, was effectively used to identify cinnamic acids in paddy rice (*Oryza sativa* L.). Rice and its lignin produced 4-methoxy and 3,4-dimethoxycinnamic acid methyl esters as the main products on pyrolysis in the presence of TMAH., 3,4,5-trimethoxy- cinnamic acid methyl ester was absent. This report describes furthermore the determination of p-coumaric and ferulic acids in rice on the basis of the yields of 4-vinylphenol and 4-vinylguaiacol produced by the conventional pyrolysis-gas chromatography method (Py-GC). The amounts of p-coumaric and ferulic acids determined by Py-GC were in good agreement with those determined by a combination of alkaline hydrolysis and high temperature.

1994-103

Sorghum, pearl millet および maize の brown midrib mutant stem 細胞壁のリグニンおよびヒドロキシ桂皮酸

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Lignin and hydroxycinnamic acids in walls of brown midrib mutants of sorghum, pearl millet and maize stems

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Abstract: The brown-midrib (bmr) mutants have been found or induced in maize, sorghum, pearl millet and hybrid of sorghum×sudangrass. We discussed the characteristics of stem walls of *bmr* mutants of sorghum (two mutants, *Sorghum bicolor*), pearl millet (*Pennesetum glaucumi*) and maize (*Zea mays*) focusing on linkage types of hydroxycinnamic acids to wall polymers and on lignin structural feature. Lignin content of all mutants determined using acid detergent lignin (ADL) procedure was significantly lower than that of normal counterparts, however there are no significant differences in lignin content determined by acetyl bromide procedure between *bmr* and normal strains, suggesting the incomplete polymerization of lignin molecules during lignification in *bmr* mutants. No etherified *p*-coumaric acids were found in all samples tested except on normal strain of pearl millet, the amounts of etherified ferulic acid in *bmr* mutants, which probably form ester-ether bridges between lignin and polysaccharides, were not as much as those of normal counterparts. The low content of the bridges in *bmr* mutants may contribute to the high rumen digestibilities.

1994-104

小麦 straw およびクスの木から抽出したリグニンの ESR

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Electron spin resonance study on lignins from wheat straw and camphor tree

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Abstract: Milled straw or milled wood lignins and dioxane lignins were isolated successively from wheat straw and camphor tree. Saponification and acidolysis were used to release ester and ether linkages, respectively, between lignins and polymetic compounds. EIectron spin resonance (ESR) spectra of the lignins isolated from each steps were measured at pH 13.0 or 12.5 under argon atmosphere or after air-bubbling in solutions. When air was bubbled in solutions, milled wood lignin from camphor tree showed an ESR signal due to 4-hydroxyphenyl group, while dioxane lignin showed

ESR signals due to 3-methoxy-4-hydroxyphenyl (guaiacyl) group and 3,5-dimethoxy-4-hydroxy- phenyl (syringyl) group. Wheat straw lignin showed a guaiacyl signal and a slight amount of syringyl signal by the air oxidation. The results confirm that lignins are polymerized with successive, sinapyl alcohol, coniferyl alcohol, and p-coumaryl alcohol when three precursors present simultaneously in a cell.

1994-105
白色腐朽菌のリグニン分解に関与する酵素系に関する研究（IV）～白色腐朽菌の還元能について
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Studies on ligninolytic enzymes of white-rot fungi (IV), Reducing ability of white-rot fungi
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Abstract: To clarify reduchg ability of white-rot fungi, we used 6 tetrazorium salts which were well-hown as dehydrogenase-detectable agents. We examined the effect of various culture conditions on fungal reducing and oxidizing activity which were detected by colorization of the tetrazorium salts and the decolorization of Poly R-478, respectively. The highest level of reducing activity of white-rot fungi was detected in nutrient-rich conditions although the decolorization of Poly R-478 was observed in nutrient-poor conditions.

1994-106
組み換え DNA によるマンガンペルオキシダーゼ変異株の作成とその諸性質
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Homologous expression and site-directed mutagenesis of recombinant manganese peroxidase in *Phanerochaete chrysosporium*
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Abstract: Homologous expression and site-directed mutagenesis on Mn^{II} ligands of manganese peroxidase (MnP) in *Phanerochaete chrysosporium* were performed using glyceraldehyde-3- phosphate dehydrogenase (*gpd*) primary metabolic promoter and polymerase chain reaction (PCR). The recombinant proteins were expressed and secreted under primary metabolic growth conditions. The Mr and absorption spectra of the recombinant MnP proteins were essentially identical to the wild type MnP. Steady state kinetic values for the oxidation of Mn^{II} by recombinant wild type MnP and wild type MnP were also very similar. In contrast, the mutation at Mn^{II} binding site resulted in markedly lower affinity and reactivity for Mn^{II}.

1994-107
リグノスチルベン-α,β-ジオキシゲナーゼアイソザイム遺伝子のクローニング
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東京大学農学部
Cloning of a lignostilbene-α,β-dioxygenase isozyme gene from *Pseudomonas paucimobilis* TMY1009
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Abstract: The gene of lignostnbene-α,β-dioxygenase I (LSD-I), one of LSD isozymes, has been cloned and expressed in *E. coli*. Since there has been no other gene of LSD isozyme around LSD-I gene, genomic library was newly constructed. Detection of LSD isozyme gene was done with universal probe forα,β□γsubunits, which compose LSD isozymes. The positive clone was analyzed by southern blot hybridization. The *BamHI-HindIII* 4.2kb fragment, containing LSD isozyme gene, was subcloned in pUC118. The gene was expressed in *E. coli* by the use of *lac* promoter. The product was purified in the purity showing single band on

PAGE. And it was identified as LSD-III on native-PAGE and reversed-phase HPLC by comparison with LSD-I. Furthermore the nucleotide sequence of the gene accorded with the amino acid sequences of two peptides from digested β subunits.

1994-108

樹木 OMT 遺伝子の構造とその発現様式の解析

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Structures and expression analysis of O-methyltransferase genes from woody plant

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Abstract: We isolated two genes encoding O-Methyltransferase from *Poplus kitakamiensis*. The Genomic clone g26 consists of four exons divided with three introns. And another clone, g25 consists of five exons divided with four introns and it shared higher homology with OMT CDNA from *P. kitakamiensis*. RNA blot analysis using gene-specific probes shows that the CDNA accumulates in young stem tissue, but g26 expresses in young leaf. The difference of expression pattern of genes demonstrates that OMT genes are developmentally regulated in the tissue-specific manners.

1994-109

PAL 活性の阻害は二次壁の木化にどのような影響を及ぼすのか？ ヒャクニチソウ単難葉肉細胞培養系を用いて

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Inhibition of PAL activity by 2-aminoindan-2-phosphonic acid (AIP) caused the depression of lignin content of secondary wall thickening isolated *Zinnia* mesophyll cell

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Abstract: Isolated mesophyll cells from the first leaves of *Zinnia elegans* L. cv. Canary Bird can be induced to differentiate into tracheary elements, which can give us a lot of biochemical events during the course of secondary thickening and lignification. The influence of AIP, an inhibitor of PAL on lignin formation was observed under a TEM and an UV microscope. At 96 hr, the differentiation into tracheary elements had almost finished, the secondary walls were lignified completely and showed the electron opaque material covered the fibrilar texture observed at 72 hr. These walls gave the absorption maxima about 280nm. Secondary walls inhibited PAL activity by AIP at 100 □M presented greatly different images as if they were cracked. They showed weak UV absorption and quite different UV absorption spectra. At 54 hr of culture, coniferyl alcohol at 100 □M were administered after inhibition of PAL activity by AIP, then the secondary walls were given the UV absorption maxima as much as the secondary walls normally cultured, indicating that the secondary walls were artificially lignified by the exogenous monolignol.

1994-110

モノリグノールグルコシドの樹幹内分布

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Distribution of monolignol glucosides in tree

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Abstract: Quantitative analyses were made on monolignol glucosides in 50% EtOH extracts from different tissue fractions of *Pinus thunbergii*, *Ginkgo biloba* and *Magnolia kobus* in May, June and August. In gingko and pine, coniferin existed mainly in the xylem, and the content was highest in May and lowest in August. In magnolia, large amount of coniferin and syringin was contained even in the bark. and the content of syringin in August was much higher than that in other season. As the distance from tip became longer, the syringin/coniferin ratio became higher, especially in the bark.

1994-111
Arctium lappa のリグナン生合成酵素
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Lignan synthesis by cell-free extracts of *Arctium lappa*
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Wood Research Institute, Kyoto University

Abstract: Cell free extracts from *Arctium lappa*. catalyzed the formation of secoisolariciresinol and lariciresinol, when incubated with coniferyl alcohol in the presence of NADPH and H2O2. Since *A. lappa* grows very well, the plant can be used as a plant material for the study of lignan synthesizing enzymes.

1994-112
(＋)-*Erythro*-(4,7-dihydroxy-3-methqxy-1”-allyl-3’,5’-dimethoxy)-8-*O*-4’-neolignan の生物変換とその変換物の抗菌活性
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Biotransformation and antibacterial activity of (+)-*erythro*-(4,7-dihydroxy-3-methoxy-1”-allyI-3’,5’-dimethoxy)-8-*O*-4'-neolignan
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Faculty of Science and Engineering, Kinki University

Abstract: The biotransformation of an acyclic neolignan, (+)-*erythro*-(4,7-dihydroxy-3-methoxy-1"-allyl-3',5'-dimethoxy)-8-*O*-4'-neolignan (1) in rat and fecal intestinal bacteria *in vitro* have been investigated. The sole metabolic product which excreted to feces (>98%) and urine (<2%) was identified as (+)-(4-hydroxy-3-methoxy-1'-allyl-3',5'-dimethoxy)-8-O-4'-neolignan (**2**) by the spectroscopic methods. Although rat and fecal intestinal bacteria could transform **1** to **2**, several tested microbes which can oxidize lignans and terpenoids could not transform **1**. The antibacterial activities of **1** and **2** were also investigated and revealed that both compounds showed to be antibacterial against several microbes.

1994-特別講演
フェニールプロパノイドと植物保護
谷口東二
九州大学農学部
Invited Lecture: The role of phenylpropanoids in plant protection and plant growth regulation
Eiji Taniguchi
Faculty of Agriculture, Kyushu University

Abstract: A wide variety of phenylpropanoids, including flavonoids and tannins etc., is considered as very important ecochemicals in the enviromental ecology. For example, the fluvic acid, producing from the plant residues in the soil and partially from lignin-like materials, may takes a role of iron-transportation from terrestrial to aquatic environment, where a rich biosphere is brought in by nourishing algae. In plant-parasite relationship, a sort of flavonoids has been revealed to be the signal compound of host plant for the parasite, and some of phytoalexins are old-known pterocarpanoids. Allelopathy is also largely caused by phenylpropanoids and their related compouunds. From the chemo-ecological point of view, the importance of phenylpropanoids for plant protection and regulation will be discussed by presenting two brief stories concerning with an insecticidal neolignan of the genus *Phryma* and an auxin-transport inhibitor as a chalcone analog.

1994-201
常温硬化クラフトリグニン接着剤の製造に関する研究
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Preparation of kraft lignin-based cold setting adhesives
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Abstract: The utilizaion of softwood kraft lignin in one of the main substrate of cold setting wood adhesives was investigated. Kraft lignin, formaldehde-phenol-kraft lignin copolymer (LP-resin) and resorcinol-terminated LP-resin (LPR-resin) were prepared as described in the 38th Lignin Symposium

(Takarnatsu). When 5-10% methanol were added to the LPR-resin solution with a solid content of 45% containing small amounts of paraformaldehyde, the mixture developed the excellent strength properties for cold-setting wood adhesives. Furthermore, LP-, LPR- and resorcinol- formaldehyde-resins were characterized by thermal analyses.

1994-202

リグニン及び糖蜜含有型ポリウレタンフォームの物性

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Thermal and mechanical properties of polyurethanes containing lignin and saccharides

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Abstract: Polyurethane (PU) foams were prepared by the following procedures. An ethylene glycol (EG) solution of kraft lignin (KL) was mixed with polyethylene glycol (PEG), and then the obtained solution was reacted with diphenylmethane diiisocyanate (MDI) in the presence of small amounts of water, silicone surfactant and tin catalyst. PU's containing molasses (MOL) were also prepared according to the above procedures. Thermal properties of PU's were studies by thermogravimetry (TG) and differential scanning calorimetry (DSC). Mechanical properties were also studied by compression tests. The effect of the addition of KL, MOL and EG to PU's on physical properties were studied.

1994-203

未晒し酢酸パルプの化学修飾による分子会合体の調製（I）残存リグニンをコアとする誘導体のセルフアッセンブリー

橋田　光、浦木康光、佐野嘉拓

北海道大学農学部

Preparation of unbleached acetic acid pulp derivatives to form self-aggregates in water by chemical modification (I), Self-assembly of the pulp derivatives centered around residual lignin as cores

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Abstract: Self-assembly or aggregation of polymer amphiphiles and hydrophobically associating water-soluble polymers is of great interest with respect to biological application and novel industrial importance. In this study, the preparation of self-aggregates in water from acetic acid plup (AWP), which contained larger amount of lignin than unbleached kraft pulp, by chemical modification was investigated to develop new functional materials from lignocellulose. Hydroxypropyl (HP)-AWP was indicated to form the aggregates in aqueous solution by transmission electron microscopic observation. On the other hand, HP-bleached AWP and commercial HP-cellulose were not found the phenomena. Furthermore, carboxymethyl-AWP did not also form the aggregate. These suggested that the AWP derivatives involving hydrophilically nonionic functional group self-assembled in water as cores of the hydrophobically residual lignin.

1994-204

化学変性した工業リグニン中のフェノールカルボン酸型構造の抗菌活性

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福井工業大学工学部

Antibiotic activity of phenol carboxylic acid type structure in chemically modified industrial lignin

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Abstract: (1) The antibiotic activity of phenol carboxylic acid changes with the species of micro-organisms. The activity of ester is higher than that of free carboxyl group. Methoxyl group gives negative effect toward the activity. The relative position of phenolic hydroxyl and carboxyl groups on aromatic nucleus does not give the remarkable effect toward the activity. (2) In order to give the activity to industrial lignin, the introduction of phenol carboxylic type structure has been tried by the use of sodium sulfide treatment and caustic fusion. Within the limits of this experiment so far, the ethanol soluble fraction after the fractionation of caustic fused lignin shows comparatively high antibiotic activity.

1994-205

Phanerochaete sordida YK-624 株の産生するマンガンペルオキシダーゼによるクラフトパルプの漂白

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九州大学農学部

Bleaching of kraft pulp with manganese peroxidase secreted from *Phanerochaete sordida* YK-624

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Abstract: We have previously reported that bleaching of hardwood kraft pulp with isolated manganese peroxidase (MnP) from *Phanerochaete sordida* YK-624 is possible. In the present study, supplementary experiments in various conditions were carried out to improve the method of bleaching with MnP. An optimum pH for enzyme treatment was 4.5. A maximum activity was observed when a temperature was 45ºC. In various organic acid buffers (50 mM and pH 4.5), malonate functioned most effectively as an Mn^{3+} chelator during bleaching of pulp with MnP. A surfactant was an important factor on enzyme bleaching. Enzyme treatments with H2O2-generating enzyme, glucose oxidase, had a similar effect on pulp brightness and bleachability as those with H2O2 added directly. The pulp treated with MnP had strength properties comparable with those for unbleached hardwood kraft pulp.

1994-206

An initial evaluation of the role of lignin-carbohydrate complexes in the xylanase prebleaching of kraft pulps

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Abstract: The molecular weight distribution of lignin- and xylan-containing macromolecules, that have been isolated from kraft pplps derived from aspen and spruce, was determined using size exclusion chromatography under highly alkaline conditions. A UV-vis monitor and a pulsed amperometric detector were used to monitor the elution of lignin and carbohydrates, respectively. The change in molecular weight, as a result of treatment with xylanase and acid was evaluated in order to examine the role of lignin-carbohydrate complexes in the xylanase prebleaching of kraft pulp. The results indicated that xylanase could decrease the molecular weight distribution of the UV-absorbing material in xylan-rich fractions obtained from kraft pulp.

1994-207

クラフトパルプの着色性キシラン画分の分離と微生物分解

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Fractionation and microbial degradation of chromophoric xylan fractions from kraft pulp

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Abstract: Unbleached kraft pulp (UKP) was degraded by a cellulase/ xylanase-bioreactor. Water-soluble chromophoric xylan was separated from the UKP by silica gel column chromatography. The fraction was characterized as follows; 1) This fraction contained more than 40% of unremovable inorganic atoms including Si, Na and S, together with non-branched xylan chain. 2) In the NMR spectrum, signals originating from olefinic carbons and methoxyl group were below background noise, suggesting that the major chromogen in this fraction is not a typical residual lignin. 3) The xylanase-resistant fraction was more effectively decolorized by microflora from soils rather than selected white-rot fungi which effectively decolorize the intact unbleached kraft pulp itself.

1994-208

酸素−アルカリ漂白過程における多糖類の分解機構（3） 酸素圧の反応選択性への影響

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Dependence of carbohydrate degradation on reaction of lignin during oxygen bleachjng (III), Effect of oxygen pressure on the reaction selectivity

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Abstract: A kinetic investigation was performed on the oxygen-alkali treatment of the mixture of carbohydrate model compound, methyl β-D-glucopyranoside (MeβG) and lignin model compound, 2,4,6-trimethylphenol (TMPh). The whole degradation pathway of TMPh was expressed by a following simple

formula.

$-d[TMPh]/dt=k[TMPh]^n$ [TMPh]: concentration of TMPh n: reaction order k: reaction constant

The amount of degraded MePG is dependent on the amount of degraded TMPh and expressed roughly by a foflowing simple formula.

MePG degradation (mol) = A x TMPh degradation (mol) A : reaction selectivity constant

1994-209

リグニンによるセルロースのオゾン分解促進

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Accelerated degradation of cellulose by the presence of lignin during ozonolysis

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Abstract: To clarify the influence of residual lignin in the kraft pulp on the degradation of cellulose, cellobiose was treated with ozone in the presence of vanillyl alcohol. When cellobiose alone was ozonized, the cellobiose was degraded linearly with the increase in supplied ozone. When cellobiose was ozonized in the presence of vanillyl alcohol, the coexisted vanillyl alcohol was completely consumed at the initial period of ozonolysis. As for the degradation of cellobiose, more degradation of the cellobiose was observed in the presence of vanillyl alcohol than its absence until ozone supply reached about 6 mmol per one mol of cellobiose. Most of the supplied ozone within this period has been consumed by the reaction with vanillyl alcohol, and the amount of ozone to attack cellobiose should be much smaller. However, the cellobiose was degraded more readily in the presence of vanillyl alcohol than in vanillyl alcohol free condition. So that we concluded that organic ozonides or hydroxy radicals formed from the reaction of vanillyl alcohol and ozone accelerated the degradation of cellobiose.

1994-210

漂白過程で生じる高分子塩素化リグニンの構造

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Structure of high molecular weight chlorolignin produced by bleaching

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Abstract: Three types kraft pulp (unbleached softwood kraft pulp, unbleached hardwood kraft pulp and oxygen prebleached hardwood kraft pulp) were chlorinated at various levels of chlorine ratio (0.1 - 0.3), and residual chlorolignins in pulps were extracted in high yields with aqueous dioxane. Extracted chlorolignins were treated by aqueous alkali under a similar condition as E1-stage of bleaching. Structural features of extracted chlorolignins and their alkali-treated products were analyzed by ^{1}H-NMR spectroscopy. These analytical results revealed that chlorolignins have structures which are quite different from usual lignin structures. Namely, only few aromatic structures are present in chlorolignins. Instead of this, chlorolignins are very rich in methyl, methylene and methine structures.

1994-211

北海道産広葉樹の連続常圧酢酸パルプ化 —酢酸パルプの漂白について—

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Acetic acid pulping of commercial hardwood chips in Hokkaido at atmospheric pressure with continuous extraction, – Bleaching of acetic acid pulp -

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Abstract: To establish the bleaching methods of acetic acid pulp with non-chlorine reagents, the pulps were prepared by extracting commercial chips of hardwood grown in Hokkaido with boiling 95% aqueous acetic acid containing 0.32% H2SO4 continuously. The pulps were bleached in PA (peracetic acid), PA-P (hydrogen peroxide) and O (oxygen)-PA-P sequence. The pulps were bleached at 62.9%, 77.9% and 90.2% brightness by using 5%PA(70ºC,30min)-3%PA (70ºC, 90min), 5%PA-3%PA-P (2% pH11, 70ºC, 2h) and O (7%NaOH, 110ºC, 60min)-5%PA (70ºC, 60min)-P, respectively. The bleached pulps were characterized by

K-values, viscosity and strength properties.

1994-212

ラジオトレーサー法によるクラフトパルプ化中のキシランの挙動の解明

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Behavior of xylan during kraft cooking studied by radiotracer technique

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Abstract: To examine the behavior of xylan during kraft cooking by radiotracer method, the wood meal in which xylan was radio-labeled selectively by feeding myo-inositol-[2-^{3}H] as a precursor to plant was treated under kraft cooking condition. Radioactivities of pulp and cooking black liquor obtained at various cooking stages were determined. The results showed that dissolution of xylan was remarkable during heat-up period and more than 70% of xylan was dissolved at this stage, and suggested that about 10% of the dissolved xylan was readsorbed on pulp fiber and this part amounts to about 25% of xylan remaining in pulp.

1994-213

リグニン誘導体添加によるバクテリアセルロース膜生産性の改善

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Improvement of the acterial cellulose production efficiency with the addition of lignin derivatives

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Abstract: ln the previous papers we have demonstrated that the addition of lignosulfonate to a bacterial cellulose medium remarkably enhanced the efficiency of the cellulose production by *Acetobacter xylinum* ATCC 10245. The highest cellulose membrane yield was 389% on the standard Hestrin-Schramm medium. In this paper the effect of the addition of kraft lignin samples has been investigated. The addition of pine kraft lignin increased the cellulose membrane yield (max. 139%) but that of birch kraft lignin affected adversely. The reason for this phenomena might have to do with the lignin structure difference and could bc a clue to find a better medium for the cellulose production.

1994-P101

白色腐朽菌ベッコウタケの染料脱色能及びリグニン分解能

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Decolorization of polymeric dye and degradation of lignin by the white-rot basidiomycete *Fomitella fraxinea*

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Abstract: Effective decolorization of polymeric dye, Poly-R by the white-rot basidiomycete *Fomitella fraxinea* was demonstrated under high nutrient carbon-high nutrient nitrogen (HCHN) conditions. This fungus also exhibited the ability to oxidatively degrade either phenolic or nonphenolic lignin model compounds under HCHN conditions. Under these conditions only laccase activity was observed, so far. The influence of the atmosphere and pH (4.5-6.5) on physiological phenomena of *F. fraxinea* was relatively minor compared to those of *Phanerochaete crysosporium*.

1994-P102

白色腐朽菌による色素の分解

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Degradation of dyes by white-rot fungi

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Abstract: Degradation of dyes by various basidionycetes was examined. Several fungi *Phanerochaete crysosporium, Bjerkandera adusta, Coriolus versicolor, C. hirsutus, C. consors, C. vellerus*, decolorized Azur B, Orange II, Congo red, Tropaeolin O and other dyes, which were added into Kirk's low nitrogen medium. However, the rate of the degradation differed in fungal strains.

1994-P103
リグニン生分解に関する研究(II) —バイオブリーチング時に産生される還元系酵素について—
片桐誠之、堤　祐司、西田友昭
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Extracellular reductive enzyme produced during biobleaching of kraft pulp by white-rot fungi
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Abstract: The role of reductive enzyme for the biobleaching of kraft pulp by *Phanerochaete crysosporium* and *Coriolus versicolor* was investigated in solid-state fermentation system with low nitrogen-high carbon and high nitrogen high carbon media. The profiles of manganese peroxidase (MnP) and reductiye enzyme productions during the biotbleaching were very different each other, suggesting the complementary function of both enzymes for the lignin degradation. Though a positive relationship between cumulative MnP activity and brightness increase was observed, any positive correlation was not observed in case of cumulative reductive enzyme activity. This result suggests that reductive enzyme may not be involved in the biobleaching of kraft pulp.

1994-P104
クラフトパルプ漂白能力を持つ木材腐朽菌のスクリーニング
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Screening of wood rotting fungi for kraft pulp biobleaching
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Abstract: Many studies about biobleaching processes are proceeding to develop new chlorine-free bleaching systems. But more efforts will be needed to overcome remaining problems for practical use. We selected several wood rotting fungi for kraft pulp biobleaching using two screening methods, Poly-R decolorization test and phenol coloradon test. 7 Fungi selected by Poly-R decolorization test show kraft pulp biobleaching ability. After 10 days treatment, the most effective fungus was able to increase the brightness from 28 to 54 and decrease kappa number from 15.7 to 6.1. 2 Fungi selected by phenol coloration test were able to increase the brightness of oxygen-alkali bleached pulp but not unbleached kraft pulp.

1994-P105
機械パルプの光による色戻りを抑制する菌のスクリーニング
河村佳枝、伊藤和貴、沖　妙、橘　燦朗
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Screening of fungi on depression of color reversion of mechanical pulps
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Abstract: Screaningg of fungi having depression of light-induced color reversion of mechanical pulps was carried out by using 2,6-dichloroindophenol and methoxy-*p*-quinone as an indicator for estimation of ability of depression of the-color reversion. First, we tried tile screaning of fungi having reducing ability of 2,6-dichloroindophenol from soils in our uniiversity forest and 67 fungi were found on Czapek-Dox agar plates. ln the second step, each 67 fungi was incubated in a liquid medium containing methoxy-*p*-quinone and 20 fungi having ability of decoloration of the quinone were obtained. ln the third step, reactivity between each an extracellular crude enzymes from the 20 fungi and methoxy-*p*-quinone was measured and screened fungi having higher reactivity. By using this method, we obtained a funguds which was called 501 had higher ability for depression of the color reversion. The fungus could be depressed 47 % of the color reversion of thermomechanical pulps.

1994-P106
Compositional changes in compost during conventional and environmentally controlled composting and growth of *Agaricus bisporus*

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Abstract: Samples from conventional, “cold” and “hot” environmentally controlled composts (“cold” and “hot” EC) taken at various stages of composting and mushroom (*Agaricus bisporus*) growth were analyzed for changes in extractives, neutral sugar composition, lignin concentration, and lignin structural features. Variable amounts of extraneous inorganic solids in the form of fine sandy particles were removed by sedimentation of the samples in a CCl4-CH2Br2 mixture. During composting, about two-thirds of the initial wall polysaccharides were consumed by compost microorganisms, and only 13-16% of the total polysaccharides were used during mushroom production. The relative lignin content of composts as measured by acetyl bromide procedure increased, both during composting and mushroom growth, and the chemical structure of lignin was altered by condensation and oxidation reactions.

1994-P107

Eucalyptus camaldulensis および *E. globulus* におけるリグニン S／G 比樹間内変異

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With-in tree variation of lignin S/G ratio in *Eucalyptus camaldulensis* and *E. globulus*

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Abstract: With-in tree variation of lignin S/G ratio was analyzed for *Eucalyptus camaldulensis* and *E. globulus* from Western Australia by using thioacidolysis method, as a link or quality breeding program. Furthermore, whole-tree values of S/G ratio and suitable sampling heights were examined from the results of each position. As a result, the differences between species and trees were recognized.

1994-P108

クラフトパルプの亜硝酸処理における脱リグニン機構（2） —亜硝酸処理におけるLCCモデル化合物の反応—

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Mechanism of delignification during nitrous acid treatment of kraft pulp (II), Reaction of LCC model compound during nitrous acid treatment

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Abstract: Much attention has been paid to nitrous acid treatment of kraft pulp as one of the non-chlorine bleaching. A nonphenolic lignin-carbohydrate complex (LCC) structure is one of the important residual lignin structures of kraft pulp. To discuss the mechanism of delignification during nitrous acid treatment, veratrylglycerol-β-guaiacyl ether (VG) and its α-ethyl ether (VGE, as an LCC model compound) were used. The reaction products observed at 90ºC suggested that the following reactions occur in the models: (1) cleavage of the Cα-Cβbond, (2) acid-hydrolysis at an α-ethyl ether (in the case of the VGE experiment). Furthermore, the identification of several unknown peaks was attempted and it is assumed that one of the unknown peaks is corresponding to a compound with carboxylic acid.

1994-P109

ベンジルエーテル結合の選択的開裂によるクラフトパルプ残存リグニンの性状の検討

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Characterization of residual lignin in kraft pulp by selective cleavage with pivaloyl iodide

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Abstract: In recent years, it has been claimed that chlorine bleaching produces various organic chlorinated compounds causing enviromental problems. Therefore, the development of pollution-free bleaching is one of the most important subjects for the pulping industry. Many studies have been reported on the chemical structures of residual lignin for the better understanding of inhibiting factors for the delignification. In this report, by the use of pivaloyl iodide (one of HASB reagents) for the selective cleavage of benzyl ether bonds under mild conditions, we tried to evaluate the contribution of benzyl ether bonds to the residual nature of lignin in kraft pulp and to characterize the lignin fraction released from kraft pulp by this treatment.

1994-P110

熱分解ガスクロマトグラフィーによるクラフトパルプ残存リグニンの構造解析 —漂白処理における変化—

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筑波大学農林工学系

Structural analysis of residual lignin in kraft pulp by pyrolysis-gas chromatography, —Changes of residual lignin during chlorine bleaching—

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Abstract: Pyrolysis-gas chromatography (Py-GC) provides useful complementary information about lignin structures to chemical degradation methods, using small amounts of samples without any sample pretreatment. Unbleached hardwood kraft pulp (LUKP) and oxygen-bleached hardwood kraft pulp (LOKP) were chlorinated at various chlorine ratios (1-5% on Pulp) , and were extracted with sodium hydroxide solution. Chlorinated kraft pulps before and after the alkali extraction were subjected to Py-GC, and structural changes of lignin in kraft pulp were studied.

1994-P111

酢酸リグニンを原料とする炭素繊維の調製(3) —酢酸リグニンの溶融性—

久保智史、沢田雅博、浦木康光、佐野嘉拓

北海道大学農学部

Preparation of carbon fiber from acetic acid lignin (III), -Fusibility of acetic acid lignin-

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Abstract: Thermal properties, especially fusibility, of acetic acid lignin (AWL) were investigated by thermomechanical analysis (TMA). On the TMA measurement of fractionated birch (B)-AWL , the fractions with less than 1,000 of molecular weight (Mw) indicated the clearly fusion state, while other fractions having larger a than original B-AWL did not fuse. Therefore, the fusibility of B-AWL was caused by low molecular weight fractions. However, abies (A)-AWL was not fused probably due to condensation of aromatic nucleus. These results suggest that the fusibility of AWL depends on not only acetylation of hydroxyl groups but also molecular structures such as condensation. Furthermore, we examined the thermal properties of industrial kraft lignin (KPL) blended with AWL. The grass-transition temperature of KPL was decreased by the addition of AWL remarkably. These results indicate that KPL may be used as thermal molding materials by blending with a small amount of AWL.

1994-P201

未晒し酢酸パルプの化学修飾による分子会合体の調製(II)～ゲスト分子との相互作用～

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Preparation of unbleached acetic acid pulp derivatives to form self-aggregates in water by chemical modification (II), - Interaction between pulp derivatives and guest molecules

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Abstract: Uptake of hydrophobic fluorescence reagents as guest molecules to self-aggregates of hydroxypropylated AWP (HP-AWP) was investigated to clarify the conjugation of the aggregates with water-insoluble materials. HP-AWP was found to have obvious transition concentration at 1.27 mg/ml corresponding to the critical micell concentration, and to form extremely hydrophobic regions in the aggregates, which was suggested by both of the remarkably shift of maximum emission wavelength and the enhancement of emission intensity. However, other derivatives having no self- assembly, HP-cellulose and carboxymethyl-cellulose, scarcely form the hydrophobic region. This suggested that the aggregates of HP-AWP took in the hydrophobic guest molecules in the hydrophobic regions which were probably formed by residual lignin in HP-AWP.

1994-P202

フェニルクマラン型二量体の配糖体化

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Glycosylation of phenylcoumaran type dimer

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Abstract: Phenylcoumaran glycoside was synthesized by linking the phenolic hydroxyl group of dehydrodiconifcrylalcohol with α-bromo-saccharides (glucose, galactose and xylose). The effects of the protecting groups on the yields were invesdgated. The glucosylation yield was increased from 30.7 % to 46.8 % by changing the protecting group of glucose from acetyl to pivaloyl. In the case of pivaloyl derivatives of galactose and xylose, the yields were 23.40% and 68.0%, respectively. For the synthesis of this phenylcoumaran glycoside, a new synthetic route was attempted with a phenyl- coumaran type dimer derived from dehydrogenation of ethylferulate.

1994-P203

リグニン前駆体とヘミセルロースの親和性

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Affinities between lignin precursors and hemicelluloses

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Abstract: In plant cell wall, a lignin is deposited in the matrix of polysaccharides through the lignification process. In this study, the binding of lignin precursors (*p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol) to hemicelluloses (from softwood and hardwood, and citrus pectin) were observed by ultrafiltration of the mixed solutions to examine the affinities between lignin precursors and hemicelluloses. As a result, the binding of lignin precursor to hemicellulose was observed in all pairs. It shows that the attractive interaction exists between them.

1994-P204

ラマン散乱スペクトルによる木材と竹のリグニン解析

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東京農業大学農学部

Raman spectroscopic identification of wood and bamboo lignin

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Abstract: Fundamental conditions to record near-infrared excited fourier-transform Raman spectra from wood meal samples were researched. Favorable Raman spectra were obtained between 150mW to 200mW of laser power with more than 100 times scanning, The size of meal samples between 20 to 200 mesh, has not affected the spectra. Under these conditions Raman spectra were recorded from meal samples and holocellulose of *Fagus crenata* B.I., *Cryptomeria japonica* D, Don and *Phyllostachys pubescens* Mazel as a typical hardwood, softwood and bamboo respectively. The Raman band intensity of *F. crenata* and *C, japonica* were decreased by the delignification process, at the wave number of 1660 cm^{-1},1600 cm^{-1}, 1460 cm^{-1}, 1330 cm^{-1},1030 cm^{-1}and 800 cm^{-1}. In the case of *P. pubescesns*, extremely strong bands observed at the wave number of 1630 and l604 cm^{-1}, and their intensity were decreased by alkaline-treatment. By the delignification process of *P. pubescens* the same bands as so *F. crenata* and *C. japonica* but 1660 cm^{-1}, and the bands at 1630 cm^{-1} and 1424 cm^{-1} were decreased. This result indicate that these Raman bands decreased by the delignification process were those of lignin origin. It was suggested that by recording Raman spectra from wood meal sample, the information of native state lignin were obtained directly and easily.

1994-P205

リグニンモデルの一電子酸化

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One electron oxidation of lignin models

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Abstract: To study the mechanism of alkaline nitrobenzene oxidation of lignin, oxidation of some lignin models, derivatives of cinnamic acid, was examined by using nitrobenzene or some oxidizing agents such as CAN and MnO2. Obtained results support a mechanism of initial oxidative decarboxylation, succeeding hydration of a side-chain double bond, and oxidation of the generated benzylic alcohol. Although one-electron-transfer mechanism is important in the oxidation step, quinone methide intermediate is also necessary because it accelerates hydration of the aryl- conjugated double bond under alkaline conditions.

1994-P206

ユーカリ属の組織化学的方法によるリグニン分析（III）—抽出条件の決定—

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Lignin analysis of Eucalyptus by histochemical methods (III), —Evaluation of the methods of alkali extraction in removing polyphenols—

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Abstract: Lignin analysis of Eucalyptus have been done by histochemical methods. However, Eucalyptus species contain a lot of polyphenols which influence on lignin analysis and thus it is required to remove those polyphenols prior to analysis of lignin. In this study, the effect of polyphenols on lignin analysis by histochemical methods were evaluated using alkali extracted samples. Specimen (cross sections and wood meals) of two Eucalyptus species were extracted by given alkali conditions and then they were analyzed by chemical arid histochemical methods. It appeared that those alkali extractives contained guaiacyl type polyphenols and affected considerably on lignin analysis, especially in vessel walls and ray cells, by histochemical methods.

1994-P207

ポプラ早生樹リグニソの化学構造について　—ヒドロキシ芳香族酸類のリグニンに対する結合様式

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Strutural feature of lignin in fast-grow and native aspen woods: Linkage types of hydroxybenzoic and hydroxycinnamic acids

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Keywords: MWL, LCC, vanillic acid, syringic acid, syringaldehyde, *p*-coumaric acid, ferulic acid, cell wall, GC-MS

1994-P208

交雑ヤマナラシ（*Populus kitakamiensis*）シンナミルアルコールデヒドロゲナーゼ（CAD）遺伝子の単離および解析

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Isolation and characterisation of genes encoding cinnamyl alcohol dehydrogenase from hybrid aspen (*Populus kitakamiensis*)

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Abstract: To change the quality and quantity of lignin, we isolated a partial gene encoding cinnamyl alcohol dehydrogenase (CAD) from hybrid aspen (*Populus kitakamiensis*) by polymerase chain reaction (PCR) method. The nucleotide sequence was analyzed and used as a probe of Southern and Northan analysis and CDNA isolation. Results showed that there was a small number of genes for CAD in the genome and CAD genes expressed in the upper and lower stem and weekly expressed in leaves. Screening of λgt 10 cDNA library, one CAD cDNA clone (1.4 Kbp) was isolated and characterized.

1994-P209

交雑ヤマナラシ・キクカミハクヨウの茎において発現するペルオキシダーゼアイソザイム遺伝子群の発現様

式の解析

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Mofecular cloning of anionic peroxidases from *Populus kitakamiensis* and Inhibition of peroxidase expression by using antisense RNA method

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Abstract: Agrobacterium-mediated gene transformtion and plant regeneration from transformed tissue were established for hybrid aspen, *Populus kitakamiensis* (*P. sieboldii* X *P. grandidentata*). Using this system, antisense *prxA1* gene driven by *prxA1* promoter that was introduced into aspen. The peroxidase activities of transformed callus were about 2-5 ford decreased. We have already isolated three cDNAs that encode anionic peoxidase from *P. kitakamiensis.* In this report, we have two genomic DNAs corresponding to the cDNAs and a novel genomic DNA that encodes anionic peroxidase. The pattern of expression of the peroxidase genes in several plant organs is discussed.

1994-P210

樹木フェニルアラニンアンモニアリアーゼ（PAL）の発現解析

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Characterization and expression of phenylalanine ammonia-lyase from populus kitakamiensis

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Abstract: In *Populus kitakamiensis*, the genes for phenylalanine ammonia-lyase (PAL) form a small gene family. Southern blot analysis indicated that PAL family was consisted with at least six members. We then isolated and characterized six PAL genes, HPAL13, *pal g1*, *pal g2a*, *pal g2b*, *pal g3*, and *pal g4*, from genome of *Populus kitakamiensis*. Furthemore, the PAL protein was isolated from the stem tissue, and analyzed using anion-exchange chromatography and 2-D gel electrophoresis detected by immuno blot. Results indicated that *M*r identical with PAL subunits was 75,000 and five subunits differing pl values were observed in the whole stem tissue. Results from Northern blot analysis suggested that *pal g1* was expressed in the young tissues near the shoot bud and *pal g2* gene-group was mainly expressed in lower stems. Thus, the expression of each PAL gene (or gene-class) from *Populus kitakamiensis* was tissue-specific and altered with the stem growth. In *Populus kitakamiensis* PAL play the important roles that are classified two groups in the function of the stem.

1994-P211

カワラタケラッカーゼアイソザイムの解析

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Characterization of laccase isoenzymes from *Coriolus versicolor*

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Abstract: Extracellular laccase is commonly produced by wood-degrading white-rot fungi. Our previous studies cleared the genetic and enzymic properties of Laccase III from *Coriolus versicolor*, and showed this enzyme was concerned in lignin biodegradation. In order to define the inherent and physiolosical role of laccase, we present to characterize the other laccase isoenzymes. Laccase l was little adsorbed on ion exchanger, thus it is considered to have a weak surface charge. So this enzyme was separated by preparative electrophoresis system, the Rotofor cell (BIO-RAD). As genetic characterization, we determined the DNA sequence of *CVLG1.*

1994-P212

担子菌のプロトプラスト調製および細胞融合によって誘導されたラッカーゼ欠損株の安定性

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The stability of laccase-less mutants induced by preparation of protoplasts and cell fusion of Basidiomycetes

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Abstract: Protoplasts were prepared from the mycelia of basidionycetes; *P. ostreatus*, *P.sajor-caju* and *P. eryngii*. In the regenerated mycelia from them, some mutants lacking laccase were induced. These mutants had no decoloring activity for carminic acid and Remazol brilliant blue R, both of which are decolorized by the parent strains. Some fusion strains with no laccase activity were produced by individual electric fusion between these laccase-less mutants or the strains with and without the laccase activit,y. These laccase-less mutants were successively cultured on an agar plate and 3 mooths, growth alteration was observed in some of their mycelia. Laccase activity of these mycelia were determined and some strains were found to have lower activities of the enzyme than the parent strains. In order to examine the possibility that the culture conditions of mycelia have caused this phenomenal, an investigation of changes in laccase activity of mycelia were made by the freeze stock method at -80 ºC and under the culture conditions using a liquid or agar medium. These results indicate that the laccase activity and the growth of mycelia were more stable for the freeze stock method.

1994-特別寄稿

「リグニン討論会の発足の頃」

九州大学名誉教授　千手諒一

第40回（1995.10.12-13）つくば 研究交流センター

1995-101

樹木のフエニルプロパノイド生合成系のチトクロム P-450 遺伝子の解析

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Molecular cloning and heterologous expression of cytochrome P-450 from a woody plant (*Populus kitakamiensis*)

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Abstract: In higher plants, some cytochrome P-450 enzymes are concerned with biosynthesis of phenylpropanoids. Cne of them, cinnamic acid 4-hydroxylase (CA4H), catalyzes the formation of *p*-coumaric acid from *trans*-cinnamic acid. The other enzyme, ferulic acid 5-hydroxylase (FA5H), catalyzes the formation of 5-hydroxyferulic acid from ferulic acid. CA4H and FA5H provide precursors for the biosynthesis of secondary metabolites, such as lignin. CA4H gene (*cyp73a*, *cyp73b*, and *cyp73c*) were isolated from *Populus kitakamiensis*, and have been determined the nucleotide sequences of their ORFs and promoter regions. Each of them has two introns. In the promoter regions of *cyp73a* and *cyp73b*, there are many *cis*-element-like sequences that ate conserved in promoters of genes involved in phenylpropanoid biosynthesis. We also isolated a CDNA (*cyp73a*) from a *P. kitakamiensis* CDNA library constructed with mRNAs of the upper part of the stem. Ushg this CDNA clone, we constructed CA4H expression plasmids for heterologous expression in yeast.

1995-102

樹木酸性ペルオキシターゼ遺伝子の組織特異杓発現様式の解析

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Tissue specific expression patterns of anionic peroxidase genes from *Populus kitakamiensis*

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Abstract: We have isolated three CDNAs (*pA2a, pA2b and pA3*) and four genomic DNAs (*prxA1, prxA2b, prxA3,* and *prxA4a*) for anionic peroxidases from *Populus kitakamiensis* and analyzed their expression patterns by using Northern blotting. The results suggested that the each gene is under the different regulation. *prxA3a* and *prxA4a* are the genes that encode anionic isoenzymes, which specifically express in stems. To identify the regulation of each gene, we analyzed the developmental expression of GUS activity in transgenic tobacco plants containing the *prxA3a*- or *prxA4a*-promoter and GUS gene fusion. The GUS activity under the control of the *prxA3a* promoter (1.0 kbp) was histochemically deteted in xylem and phloem tissues in which lignin is vigorously synthesized. In the other hand, the *prxA4a* promoter (1.1kbp) had transcriptional activity only in the auxiliary bud and leaf trace. In order to determine *cis*-acting elements which regulate complicated patterns of *prxA3*a expression, we constracted the 5 - deleted series of the promoter fragment with GUS gene and transformed plants with them.

1995-103

酵素ラッカーゼによるコニフェリルアルコール、イソオイゲノールの重合反応

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Polymerization of coniferyl alcohol and isoeugenol by laccases

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Abstract: In this paper, we wish to report dehydrogenative polymerization of isoeugenol and coniferyl alcohol by various laccases and peroxidase. Urushi laccase oxidized isoeugenol very slowly. Dimer (1), (2a,2b),

tetramer (3) and oligomer were produced, but no dehydrogenative polymer (DHP). Fungal laccase oxidized the substrate faster than urushi laccase. Peroxidase from horseradish oxidized isoeugenol even slower than the fungal laccase in the presence of hydrogen peroxide.

Compared to urushi laccase, fungal laccases oxidized coniferyl alcohol faster under the same reaction conditions. Dehydrogenative polymer obtained enzymic reaction of coniferyl alcohol and isoeugenol have been characterized by NMR analysis.

1995-104
Arctium lappa によるセコイソラリシレジノールの生合成
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京都大学木質科学研究所
Biosynthesis of secoisolariciresinoi in *Arctium lappa*
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Wood Research Institute, Kyoto University

Abstract: Cell-free extracts from *Arctium lappa* L. cv. *kobarutogokuwase* catalyzed the enantio- selectiye fortmtion of (+)-secoisolariciresinol, Then incubated with coniferyl alcohol in the presence of NADPH and H2O2. The stereochemical mechanisms sharply contrasts with that in (-)-secoisolariciresinol formation from coniferyl alcohol by enzymes of *Forsythia* plants.

1995-105
リグニン化学構造の不均一性　—エーテル結合の部分的開裂によって生成する低分子量リグニン区分の性状—
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東京大学農学生命科学研究科
Heterogeneity of lignin structure, —Properties of low molecular weight lignin formed by limited ether bonds cleavage—
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Abstract: The authors have been investigating the structural heterogeneity of lignin, in particular, heterogeneous distribution of bonding structures and aromatic structures. ln this context, a β-O-4 rich end-wise lignin fraction was found in the low molecular weight fraction of birch periodate lignin and phenylcoumaran rich lignin fraction was found in a very low yield in the TMSiI-depolymerized fraction. In this paper, a periodate lignin prepared from diazomethane- methylated wood meal was partially depolymerized by TMSiI and the low molecular weight fractions extracted by dioxane/water (9/1) were characterized. It was found that the low molecular weight fractions were rich in β-O-4 linkage and syringyl unit. This was particularly characteristic for the acetone soluble fractions.

1995-106
リグニンの酸化過程におけるシリンギルおよびグアイアシルカルボニルラジカルの生成機構　—特異的シリンギルおよびグアイアシル末端基の定量—
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Production mechanism of syrhgyl carbonyl and guaiacyt carbonyl radicals by oxidations of lignin, -Determination of syringyl and guaiacyl end-groups the bonding type of which are specific
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Kyushu Dental College

Abstract: Electron spin resonance spectra of dioxane lignins from various plants were measured at pH l3 in the presence of oxidants. Hardwood lignin and true grass lignins showed signals due to syringyl carbonyl and guaiacyl carbonyl radicals, and softwood lignins showed only very weak guaiacyl carbonyl signal. These radicals were thought to be produced by oxidative Cα-Cβ cleavage in lignins. The signal intensity was found to be due to the types of linkages of end-groups.

1995-107
DHP および β-O-4 型リグニンモデル化合物の熱分解生成物
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筑波大学農林工学系
Comparative study of pyrolysis products of DHP and β-O-4 lignin model compounds
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Abstract: This paper describes the contributions of the β-O-4 substructure in lignin to the pyrograms of lignocellulosic materials. Two β-O-4 type lignin model compounds, guaiacylglycerol-β- guaiacyl ether (GGG) and guaiacylglycerol-β-coniferyl ether (GGC), were pyrolyzed at 500 ºC for 4 s. The products were compared with those of a dehydrogenation polymer of coniferyl alcohol (DHP). The primary products of GGG were guaiacylvinylketone and (*E)*-coniferyl alcohol, together with guaiacol released by the cleavage of the β-ether bond. 4-Methylguaiacol, 4-vinylguaiacol, ioseugenol and dihydroconiferyl alcohol, the major products of DHP, were obtained in very small levels. GGC produced dihydroconiferyl alcohol, coniferaldehyde and (*E*)-coniferyl alcohol in considerable levels. Unlike GGG, GGC contributed to the formation of guaiacol, 4-methylguaiacol, 4-vinylguaiacol and ioseugenol. The pyrolysis products from the model compounds suggest that coniferyl alcohol end-groups in lignin are related to the formation of dihydroconiferyl alcohol.

1995-108
クラフトパルプの亜硝酸処理における脱リグニン機構(3)—非フェノール性 β-5 型および β-O-4 型リグニンモデル化合物における Cα-Cβ 結合の開裂—
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筑波大学農林工学系
Mechanism of delignification during nitrous acid treatment of kraft pulp (III), Cleavage of Cα-Cβbond in nonphenolicβ-5 type andβ-O-4 type lignin model compounds
Masanori Kishino, Hiroshi Ohi, Akira Yamaguchi
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Abstract: The Cα-Cβcleavage has been reported as one of the main reactions during the nitrous acid treatment of nonphenolic β-O-4 type lignin model compounds. The mechanism of Cα-Cβcleavage was discussed using a nonphenolic β-5 type lignin model compound and nonphenolic β-O-4 type lignin model compounds in which deuterium was substituted for Cα-hydrogen. The Cα-Cβbond in coumaran ring of dehydrodiisoeugenol methyl ether was cleaved giving veratraldehyde in a high yield. Thus, the cleavage of the Cα-Cβbond in the nonphenolic β-5 type lignin model compound was one of the main reactions, and it was the same as in nonphenolic β-O-4 type lignin model compounds. Veratrylglycerol-β-guaiacyl ether which had a deuterium at the Cαposition gave veratraldehyde having deuterium. The Abstraction of hydrogen was not observed during the nitrous acid treatment.

1995-109
塩素漂白過程における酸化反応の役割
幸田圭一、新谷博幸、松本雄二、飯塚堯介
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Role of oxidation reaction in the chlorine bleaching process
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Abstract: New calculation method was proposed for the evaluation of oxidation reaction and substitution reaction during chlorine bleaching. New calculation method proved that more than half of the chlorine was consumed by oxidation reaction during chlorine bleaching. As an average, about 4 electrons were abstructed from one lignin structural unit. This result coincides with our former results that chlorinated lignin contains only few aromatic structures. When oxidation reaction was depressed, delignification did not proceed effectively.

1995-110
ラジオトレーサー法によるクラフトパルプ化中のペクチンおよびキシランの挙動の解明
今井貴規[*1]、後藤任孝[*1]、松村浩如[*1]、安田征市[*1]、寺島典二[*2]
[*1] 名古屋大学農学部、[*2]USDA 林産物研究所
Behavior of pectin and xylan during kraft pulping studied by radiotracer technique
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Abstract: Pectin and xylan were labeled with ^{14}C and ^{3}H respectively by administration of D-glucuronic acid-[6-^{14}C] and *myo*-inositol-[2-^{3}H] to a growing stem of magnolia. The doubly radio-labeled wood tissue was treated under kraft cooking conditions, and radioactivities of pulps and cooking black liquors were determined at various stages of cooking. The results showed that xylan was dissolved rapidly during heat-up stage, whereas pectin could not be dissolved easily at the early stage of cooking. Readsorption of xylan on pulp was demonstrated at the late stage, whereas that of pectin was not observed.

1995-111

アバカ・ケナフの酵素処理

上垣勇吾、伊藤和貴、沖　妙、橘　燦郎
愛媛大学農学部

Enzyme treatment of non-woody fiber, abaca and kenaf

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Faculty of Agriculture, Ehime University

Abstract: Treatment of the pulps prepared from non-woody plants, abaca and kenaf with two commercially available pectinases containing CMC-ase, xylanase and β-glucosidase was conducted to investigate the effect of the pulp properties on the pectinase treatment. We found that parenchyma cells in the pulps were removed by the treatment with pectinases. We also found that physical properties, water retention value and pulp strength were improved by the treatment with pectinases.

1995-112

フェノール酸化試薬によるリグニン酸化過程における分子状酸素の役割　―モデル実験―

森下智之、松本雄二、飯塚堯介
東京大学農学部

Model experiment on the role of molecular oxygen during oxidation reaction of lignin by phenol oxidizing reagents

Tomoyuki Morishita, Yuji Matsumoto, Gyosuke Meshitsuka
Graduate School of Agriculture and Agricultural Life Science, the University of Tokyo

Abstract: When vanillyl alcohol (VA) was oxidized by laccase under pressurized oxygen (3 atm), reaction products become more hydrophilic than those obtained by the oxidation under normal pressure. ^{1}H-NMR analysis suggested that oxidation products of VA by Mn(III) under pressurized oxygen had a different structural feature from those obtained under anaerobic condition. These results revealed that oxygen can be incorporated in the reaction of phenolic compounds with one electron oxidizing reagents. When methyl-β-D-glucopyranoside (MGP) was subjected to Mn(III) oxidation together with homovanillic acid, no active species harmful to MGP was produced.

1995-113

常圧酢酸パルプ化に関する研究　―β-*O*-4 型エーテル結合の反応性―

榎　牧子、佐野嘉拓
北海道大学農学部

Acetic acid pulping of wood at atmospheric pressure. ―Reactivity of β-aryl ether linkages―

Makiko Enoki, Yoshihiro Sano
Faculty of Agriculture, Hokkaido University

Abstract: To explain the reaction mechanism of delignification by aqueous AcOH containing a small amount of HCl or H2SO4 (acetolysis), guaiacylglycerol-β-guaiacyl ether (GOG) and veratrylglycerol-β-guaiacyl ether (VOG) were refluxed in 70-95% AcOH with HCl or H2SO4. β-Ethers by acetolysis were cleavaged much more readily by acetolysis than acidolysis. R-GOG and R-VOG withγ-CH3 were prepared from GOG and VOG by tosylation, iodination and finally reduction. R-GOG and R-VOG produced guaiacol and corresponding aryl acetone as main products indicating that acetolysis for protolignin modified terminal CH2OH groups in lignin to CH3 groups is a new degradation method for the investigation on the chemical structure of lignin.

1995-特別講演

遺伝子の世界からみた生命の不思議　―つくば高血圧マウスとつくば低血圧マウスの創作―

村上和雄

筑波大学応用生物化学科
Invited Lecture: Tsukuba hypertensive mice and Tsukuba hypotensive mice
Kazuo Murakami
Institute of Applied Biochemistry, University of Tsukuba

Abstract: We have constructed the chimeric renin-angiotensin cascade in mice comprising both human renin and human angiotensinogen as well as the endogenous angiotensin-converting enzyme and angiotensin II receptor by crossmating separate lines of transgenic mice carrying either the human renin or human angiotensinogen genes. Although each single gene carrier did not develop hypertension despite the observed normal tissue specific expression of the transgenes, dual gene strains exhibited a chronically sustained increase in blood pressure (BP). The systolic BP was 130±7 mmHg. We named the hypertensive mice as “Tsukuba Hypertensive Mice". On the other hand, we generated angiotensinogen-deficient mice by homologous recombination in mouse embryonic stem cells. These mice do not produce angiotensinogen in the liver, resulting in the complete loss of plasma immunoreactive angiotensin I. The systolic blood pressure of the homozygous mutant mice was 66.9 ± 4.1 mmHg, significantly lower than that of wild-type mice (100.4±4.4 mmHg). We named the hypotensive mice as "Tsukuba Hypotensive Mice".

1995-201
白色腐朽菌の産生するマンガンペルオキシダーゼの諸特性について
原園幸一、近藤隆一郎、坂井克己
九州大学農学部
Comparison of properties of manganese peroxidases from some white rot fungi
Koichi Harazono, Ryuichiro Rondo, Kokki Sakai
Faculty of Agriculture, Kyushu University

Abstract: Properties of partially purified manganese peroxidases (MnPs) from liquid cultures of white rot fungi, the fungus YK- 505, *Phanerochaete sordida* YK- 624 and *Phanerochaete chrysosporium* were compared. Properties of MnP from *P. sordida* YK-624 were similar to those of MnP from *P. chrysosporium*, while MnP from YK-505 had different properties from those produced by two other fungi. MnP from YK-505 adsorbed onto a hardwood kraft pulp. MnPs from *P. sovdida* YK-624 and *P. chrysosporium* did not significantly adsorb onto the pulp. MnP from YK-505 was superior to MnPs from *P. sordida* YK-624 and *P. chrysosporium* in stabilities against high temperature and high concentration of H2O2.

1995-202
アルカリ性木粉培地に生育する微生物が生産するフェノールオキシダーゼについて
国沢直子、近藤隆一郎、坂井克己
九州大学農学部
Characterization of phenoloxidases from new isolates which can grow on alkaline wood meal media
Naoko Kunizawe, Ryuichiro Kondo, Kokki Sakai
Faculty of Agriculture, Kyushu University

Abstract: We found several fungi producing extracellular phenol oxidases on alkaline wood meal media. These crude phenol oxidases had optimal pH near neutral when guaiacol was used as a substrate. These enzymes were produced well on alkaline wood meal media, but hardly on well-known laccase-inducing media. Active fractions were obtained by ion-exchange chromatography, and the fractions revealed several bands of activity at pH 4.6 and 8 on non- denaturing PAGE, but culture filtrate of *Coriolus versicolor* revealed active bands only at pH 4 and 6.

1995-203
カワラタケラッカーゼアイソザイムの解析
三国順子[*1]、中村雅哉[*2]、川合伸也[*1]、片山義博[*3]、諸星紀幸[*3]
[*1]東京農工大学農学部、[*2]森林総合研究所、[*3]東京農工大学生物システム応用科学科
Characterization of laccase isoenzymes from *Coriolus versicolor*
Junko Mikuni[*1], Masaya Nakamura[*2], Shinya Kawai[*1], Yosbihiro Katayama[*3], Noriyuki Morohoshi[*3]
[*1]Faculty of Agriculture, Tokyo University of Agriculture and Technology, [*2]Forestry and Forest Products Research Institute, [*3]Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology

Abstract: Our previous studies showed laccase III concerned in lignin biodegradation, and cleared the

properties of this enzyme genetically and enzymatically. In order to define the inherent and physiolosical role of laccase, we present to characterize the other laccase isoenzymes. As genetic characterization, we sequenced another laccase gene and named CVLG1, previously. In this study, the origin of Laccasc III gene and CVLG1 were confirmed by Southern hybridization. Two Pst I DNA fragments were hybridized by probe a and b, respectively. These four fragments were analyzed.

1995-204

土壌微生物 *Pseumomonas paucimobilis* SYK-6 のリグニン・ビフェニル特異的脱メチル化酵素遺伝子に関する研究

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Analysis of the lignin-biphenyl specific demethylase gene from *Pseudomonas paucimobilis* SYK-6

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Abstract; *Pseudomonas paucimobilis* SYK-6 is able to grow on DDVA and other various lignin dimeric compounds as a sole carbon source. To study of the specific reactions of lignin degradation by the microorganism, we investigate the degradation of the biphenyl compound, DDVA, by *P. paucimobilis* SYK-6. In our study, we analyzed the demethylation of DDVA, which is the first step of DDVA degradation. We isolated a deficient mutant (NT-1) for DDVA demethylation, and the 6kbp-fragment from *P. paucimobilis* SYK-6 chromosomal DNA, which complemented DDVA demethylation for NT-1. Here we report characteristics of this 6kbp-fragment.

1995-205

土壌微生物 *Pseumomonas paucimobilis* SYK-6 のリグニン・ビフェニル特異的環開裂酵素遺伝子の構造と機能に関する研究

片山義博[*1]、花城　薫[*1]、川合伸也[*2]、諸星紀幸[*1]、江頭　崇[*3]、彭　学、金原和秀[*4]、政井英司[*3]、　福田雅夫[*4]、矢野圭司[*4]
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Cloning and characterization of the gene encoding novel ring cleavage enzyme for lignin biphenyl compuond in *Pseumomonas paucimobilis* SYK-6

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Abstract: The soil bacterium, *Pseumomonas paucimobilis* SYK-6 is able to degrade various types of dimeric lignin compounds such as biphenyl, β-aryl ether, phenylcoumaran etc. Here, we reported molecular cloning of the gene encoding ring cleavage enzyme for lignin biphenyl. The 1.5 Kbp DNA fragment which maintained the ring cleavage activity was identified by subcloning and sequencing. An open reading frame encoding 334 amino acid was identified which designated lig Z. The lig Z gene was expressed in *E. coli* and the characterization of this enzyme was carried out. The enzymatic activity was observed only when OHDDVA (2.2'.3-trihydroxy-3'-methoxy-5,5'-dicarboxybiphenyl) was used as substrate but not for protocatechuate, 3-methylgallic acid and 2.3-dihydroxybiphenyl.

1995-206

α 位にカルボニル基を有する難分解性 β-O-4 型リグニンモデル化合物のマンガン及びシユウ酸による分解

近藤　登、服部武文、島田幹夫
京都大学木質科学研究所

A novel MnP-mimetic breakdown of recalcitrant nonphenolic lignin model compounds with two electron pulling groups in the presence of Mn(III) and oxalate

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Wood Research Institute, Kyoto University

Abstract: Nonphenolic dimeric lignin model compounds with two electron-pulling groups such as 1-(4-ethoxy-3-methoxyphenyl)-2-(4-fomyl-2-methoxyphenoxy)-1-ethanone (I) was broken down with Mn(III)

in the presence of oxalate and dimethyl sulfoxide (DMSO), yielding the Cα-Cβbond cleavage and Cβ-ether bond cleavage products such as 4-*O*-ethylvanillic acid (II) and vaniliin (III), respectively. ln this case, one atom of dioxygen has been demonstrated to be incorporated into the product (II). Almost no cleavage reaction occurred in the control systems without either Mn(III), oxalate or DMSO. Possible mechanisms for these unprecedent degradation of lignin models are discussed.

1995-207

担子菌由来リグニン分解酵素の有機溶媒中における反応

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Reaction of ligninolytic enzymes from basidionycete in organic solvents

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Wood Research Institute, Kyoto University

Abstract: Oxidation of aromatic compounds by lignin peroxidase (LiP) of *Phanerochaete chrysosporium* was examined in organic solvents. LiP exhibited high activity of 3.3'-dimethoxy- benzidine oxidation in several 70% aqueous solutions of water-miscible solvents including ethylene glycol, diethylene glycol, methylcellosolve, and acetone. LiP catalyzed the oxidation of several phenolics and aromatic amine including 3,3'-dimethoxybenzidine, catechol, *o*-phenylenediamine and *o*-aminophenol in 70% aqueous ethylene glycol solution. UV/VIS absorption analysis suggested the formation of an intermediary charge-transfer complex in the reaction in water, whereas the presence of this complex was not shown in the 70% aqueous ethylene glycol media. Electron spin resonance (ESR) analysis demonstrated that the reaction proceeded *via* the cation radical of 3,3'-dimethoxybenzidine both in water and 70% aqueous ethylene glycol solution.

1995-208

リグニン生分解に関する研究（IV） —針葉樹および広葉樹クラフトパルプのバイオブリーチングにおけるマンガンペルオキシダーゼとリグニン分解の関係—

片桐誠之、江原克信、堤　祐司、西田友昭
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Studies on lignin biodegradation (IV), —The relationship between manganese peroxidase and delignification on biobleaching or softwood and hardwood kraft pulp—

Nobuyuki Katagiri, Katsunobu Ehara, Yuji Tsutsumi, Tomoaki Nishida
Faculty or Agriculture. Shizuoka University

Abstract: The reladonship between MnP and delignification on biobleaching or softwood (SWKP) and hardwood kraft pulp (HWKP) was investigated. The treatment of SWKP and HWKP with partially purified MnP supports that MnP can bleach SWKP and HWKP, and lignin loss of SWKP and HWKP by MnP is nearly same level. ln the biobleaching of HWKP, there was a linear relationship between brightness increase (lignin loss) and cumulauve activity of MnP produced by *Phanerochaete chrysosporium*, *Trametes versicolor* and lZU-l54. In the biobleaching of SWKP, though lignin loss was same level, cumulative activity or MnP produced by *Phanerochaete chrysosporium* was much less than by IZU-154. These results suggest that other enzymes may contribute to delignification of SWKP during treatment with *P. chrysosporium*.

1995-209

白色腐朽菌のリグニン分解に関与する酵素系に関する研究（VII）—クラフトパルプのバイオブリーチングにおける白色腐朽菌の還元能の役割—

平井浩文、北濱　孝、近藤隆一郎、坂井克己
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Studies on ligninolytic enzymes of white-rot fungi (VII), —The role of reducing abilities of white-rot fungi during biological bleaching of kraft pulp—

Hirofumi Hirai, Takashi Kitahama, Ryuichiro Kondo, Kokki Sakai
Faculty of Agriculture, Kyushu University

Abstract: We examined biological bleaching of unbleached hardwood kraft pulp (UKP) with *Phanenochaete sordida* YK-624 and *Phlebia* sp. YK-63. P. sordida YK-624 secreted oxalate during the biological bleaching of UKP under the condition of the initial culture pH 7.0, and then the culture pH was dropped to about 5.0. After 2days incubation, the culture pH being dropped, the brightness increase of

fungal-treated UKP and MnP producbon were observed. *Phlebia* sp. YK-663 could not bleach UKP at initial culture pH 7.0, and neither the drop of pH nor MnP production were observed. Mn^{2+} ion was detected in UKPs which were brightened by each fungus although *Phlebia* sp. YK-663 could not reduce manganese dioxide present in UKP under the initial culture pH 7.0. It is expected that the ability of droppinng culture pH and MnO2-reducing ability are necessary to delignify residual lignin in UKP, and that these abilities were related to the reducing ability detected with tetrazolium salts.

1995-210

$MnSO_4$ 無添加系でのマンガンペルオキシダーゼによるクラフトパルプの漂白

原園幸一、近藤隆一郎、坂井克己
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Bleaching of kraft pulp with manganese peroxidase without addition of MnSO4

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Faculty of Agriculture, Kyushu University

Abstract: *In vitro* bleaching of an unbleached hardwood kraft pulp was performed with partially purified manganese peroxidase (MnP) from the fungus *Phanerochaete soldida* YK-624 without the addition of MnSO4 in the presence of some organic acids. When the pulp was treated without the addition of MnSO4, the pulp brightness increased by about 10 points in the presence of 2 mM oxalate while the brightness did not significantly increase in the presence of 50 mM malonate, a good Mn^{3+} chelator. Cxalate reduced MnO2 which had been existed in the pulp or produced from Mn^{2+} by the oxidation with MnP, and supplied Mn^{2+} to MnP system. It can be concluded that bleaching of hardwood kraft pulp with MnP by the effective use of manganese originally present in the pulp was possible in the presence of oxalate, a good Mn^{3+} chelator and MnO2-reducing agent.

1995-211

PEG および PEG−PPG 系リグニン／糖ベースポリウレタンの熱分析

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Thermal analysis of polyurethanes from PEG- and PEG-PPG-/lignin and saccharide systems

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Abstract: Polyurethane (PU) foams were prepared by the following procedures. A 50 wt% solution of kraft lignin (KL) in polyethylene glycol 200 (PEG, m.w. 200) was mixed with PEG 200, and then the obtained solution was reacted with diphenylmethane diiisocyanate (MDI) in the presence of small amounts of water, silicone surfactant and tin catalyst. PU foams were also prepared using a PEG- polypropylene grycoI (PPG) copolymer instead of PEG 200 in the above process. Furthermore, PU's containing molasses (MOL) were also prepared according to the above procedures. The thermal properties of PU’s were studied by differential scanning calorimetry (DSC), thermogravimetry (TG) and TG-infrared spectrometry (FTIR). The influence of the addition of KL and MOL to PU's on thermal properties were studied.

1995-212

リン酸化によるリグノセルロースのヒドロゲル化

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Hydrogelation of lignocellulosic materials by phosphorylation

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Abstract: To investigate the swelling mechanisn with crystalline and fine structures, the chlorite-treated woodmeal and the ramie fiber were pretreated with hydrochloric acid or sodium hydroxide and by intensive milling. The phosphorylated product obtained from the milled ramie showed the water absorbency 17 (g H2O/g). The treatment with HCl or NaOH being followed by phosphorylation decreased the water absorbency of the product prepared from the woodmeal. The phosphorylated product was identical with Cellulose I regarding the crystalline structure. Consequently, the phosphorylation occurs on the finer structure unit such as microfibril. The stronger hydrogen bond between microfibrils of the ramie decreases the water absorbency of the product.

1995-213

ベンジル化木材の単独発泡における含有 LCC の効果

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Effects of lignin-carbohydrate complexes on foaming of benzylated wood without adding plasticizers

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Abstract: Researches have been done aiming to make a degradable foam from benzylated wood. As a result we have found that it is possible to produce a expandable benzylated wood without adding any of plasticizers or other polymers and also it is necessary for the benzylated wood to retain more than 70% of the LCC in the original wood in order to accomplish ten to twenty times foaming. There was direct proportional relationship between the foaming extents and LCC contents of the resin up to nine-teen times of foaming extent. What kinds of effects of lignin have been brought on physical properties of the final products also have been investigated.

1995-P01

モノリグノールグルコシドの樹幹内分布と季節変動

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Distribution and seasonal changes of monolignol gucosides in *Magnolia kobus*

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Abstract: Monolignol glucosides (MLG), coniferin (CF) and syringin (SY), existed in the xylem and the bark of *Magnolia kobus* in different season were determined quantitatively. The proportion of SY in the bark were much higher compared with that in the xylem. The concentration of CF was a higher value in lignifying season. But even in a resting stage, SY content in the bark was very high. In lignifying season, MLG in the outer bark was almost syringin, on the contrary, in the cambial zone and differentiating xylem was almost coniferin. It seems that CF existing in the xylem is related to the lignification of stem. But there is no relationship between SY content and lignification of xylem in magnolia shoot.

1995-P02

芳香環 3 位あるいは 5 位に水酸基を導入したモノリグノールクルコシドのコブシ樹幹内での挙動

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Bahavior of monolignol glucoside derivatives which contains hydroxyl group on aromatic ring 3- or 5-position in magnolia shoot

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Abstract: The feeding of hydroxylated monolignol glucoside to magnolia shoot revealed that these derivatives can be used as precursors of coniferin and syringin, and the structural conversion proceeds mostly to the direction of the increase of methoxyl groups. The mechanism of the conversion seems to need a temporary removal of glucose residue, in spite of our previous result [1]. By the further study using variously labeled coniferin, it became clear the conversion from coniferin to syringin is achieved at the stage of monolignols, not their glucoside.

1995-P03

交雑ヤマナラシ キタカミハクヨウから単離した OMT 遺伝子の解析

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Analysis of genes for OMT that were isolated from a hybrid aspen, *Populus kitakamiensis*

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Abstract: *O*-methyl transferase (OMT) plays a important role in monolignol biosynthesis. Genomic Southern blot analysis suggested that the genes for OMT formed small gene family in *Populus kitakamiensis*.. We have isolated two genes, *homt1* and *homt3*, from genome of *P. kitakamiensis*.. Two OMT isoenzymes have been isolated from stems or *P. kitakamiensis*. They differed from one another in substrate specificity. It is important to clarify the relationship between the genes and isoenzymes. We attempted to express the genes in *E. coli* cells and *P. kitakamiensis*. On the other hand, antisense gene for OMT was introduced into tobacco and the transformants were regenerated into plants.

1995-P04

ゴマ (*Sesamum indicum*) のフロフラン型リグナンの生合成

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Biosynthesis of furofuran lignans in sesame (*Sesamum indicum*)

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Abstract: Sesame seeds contain furofuran lignans such as (+)-sesamin and (+)-pinoresinoI, which are widely distributed in higher plants. To investigate biosynthesis of the furofuran lignans in sesame (*Sesamum indicum*), [8-^{14}C]coniferyl alcohol was fed to excised stems of sesame and [8-^{14}C]coniferyl alcohol was incubated with insoluble residue from stems and capsules, upon removal of soluble enzymes, in the absence of cofactor and in the presence of NAD-malate or aqueous Kl. Fllowing [8-^{14}C]coniferyl alcohol administration to excised shoots for 3 hr, radio-labeled pinoresinol was formed more in stems than in leaves. The (+)/(-) ratio was 42-46 : 58-54. Radio-activities for sesamin and sesamolin were the same as background level. Enzymatic [8,8'-^{14}C]pinoresinol formation with the insoluble residue was found in each incubation condition. The addition of NAD-malate enhanced the pinoresinol formation.

1995-P05

カラスザンショウ（*Zanthoxylnum ailanthoides*)のリグナンの生合成と立体化学

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Lignans biosynthesis and stereochemistry of *Zanthoxylum ailanthoides*

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Abstract: Adninistration of [8-^{14}C]coniferyl alcohol to an excised shoot of *Zanthoxylum ailanthoides* resulted in a conversion of pinoresinol (almost racemic), (-)-lariciresinol (71%ee), and (+)-secoisolariciresinol (56%ee). (±)-[8,8'-^{14}C]pinoresinols was incubated for 1 hr with cell-free extracts from *Z. ailanthoides* in the presence of NADPH. Both [8,8'-^{14}C]lariciresinol and [8,8'-^{14}C] secoisolariciresinol were detected as (+)-forms. Time-course experiments (5, 20min, 1 hr) using the cell-free extracts [10-80% (NH4)2SO4, precipitate under the same condition as above showed formations of lariciresinol and secoisolariciresinol were linear over the time period, corresponding a linear depletion of pinoresinol.

1995-P06

反芻家畜の消化作用により可溶化したイネ科牧草リグニンの特性

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Structural characteristics of soluble lignin fractions released by digestion in ruminant animal from forage grasses

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Abstract: Faecal soluble lignin (FSL), extracted from the faeces of sheep that received orchard grass and

timothy, were compared with 90% dioxane-soluble lignins released by ball milling (MHL) and by subsequent enzymatic hydrolysis (EHL) from the same grasses. FSL contained much less carbohydrate and esterified *p*-coumaric and ferulic acids than MHL and EHL. Molecular weight of FSL was much smaller than those of MHL and EHL. The molar ratio of syringaldehyde to vanillin produced by nitrobenzene-oxidation was higher for FSL than for MHL and EHL. Results indicated that syringyl-rich lignin fragements with less phenolic acid esters were released by digestion in sheep from the forage grasses.

1995-P07

白色腐朽菌のリグニン分解に関与する酵素系に関する研究（VIII）—*Phanerochaete sordida* YK-624 株によるベラトリルアルコールの生産について—

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九州大学農学部

Studies on ligninolytic enzymes of white-rot fungi (VIII), — Production of veratryl alcohol by *Phanerochaete sordida* YK-624 —

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Abstract: To clarify the production of veratryl alcohol (VA) by *Phanerochaete sordida* YK-624 under the nutrient-rich conditions, where the reduction of tetrazolium salts was induced and no lignin peroxidase activity was detected, the pathway for VA biosynthesis was examined by the addition of cinnamic acid (Cacid) as the precursor of VA to potato-dextrose media. (pH 7.0). Cacid was transformed to cinnamaldehyde (Cald), cinnamyl alcohol (CA), benzaldehyde (Bald), and benzyl alcohol (BA) by *P. sordida* YK-624, and no benzoate was detected. It was suggested that the pathway for VA biosynthesis in *P. sordida* YK-624 differed from the pathway proposed by Jensen *et al*. *Phlebia* sp. YK-663. which showed lower tetrazolium salts-reducing activity than *P. sordida* YK-624 and hardly produced VA under ligninolytic or nutrient-rich conditions, transformed Cacid to Cald and CA, but Bald and BA were hardly detected.

1995-P08

リグノスチルベン-α,β-ジオキシゲナーゼアイソザイム I および III のキメラ酵素の基質特異性（II）

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Substrate specificities of chimera enzymes of lignostilbene-α.β-dioxygenase isozyme I and III, (II)

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Abstract: *Pseudomonas paucimobilis* TMY1009 produced at least four lignostilbene-α,β- dioxygenase (LSD) isozymes. LSD-I and -III were composed of two homogeneous α and β subunits, respectively. LSD-I degraded 4, 2'-dihydroxy-3, 3'-dimethoxy-5-(2"-carboxyyinyl) stilbene (β-5 stilbene) very slowly. It seemed to be specific for 4, 4'-dihydroxy-3, 3'-dimethoxystilbene (β-1 stilbene). The other hand, LSD-III degraded β-5 stilbene better than β-1 stilbene. The gene of LSD-I (*lsd* A) and -III (*lsd* B) were cloned and sequenced. These two isozymes share 69% amino acid sequence identity, yet differ markedly with respect to their substrate specificities. Chimeric LSD consisting of either the N-terminal fragment ofαsubunit fused with the C-terminal fragment of β subunit or the inverse pair. Chimera α158 βincludes the 158 N-terminal residues of αsubunit fused to the complementary part of the βsubunit sequence. Chimera βl58α,β356α and α407βwere designed in the same way. Analyses on Km and specific activities for two stilbenes indicated that chimera α158βand βl58αhave the same substrate specificities as LSD-III (β subunit) and LSD-I (αsubunit), respectively. As concerns β356α and α407β, no activity was detected. Further investigation is required.

1995-P09

種々の培養条件下における白色腐朽菌 *Phanerochaete chrysosporium* のフエニルアラニンアンモニアリアーゼ（PAL）活性

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The detection of PAL activity in *Phanerochaete chrysosporium* grown in the four different cultures

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Abstract: The activities of L-phenylalanine ammonia-lyase extracted from *Phanerochaete chrysosporium*

which had been grown in the four different cultures (HC-LN, HC-HN, LC-MN, and LC-HN) were assayed. The PAL activity and the concentration of veratryl alcohol in the culture fluid were greater in HC-LN culture than in HC-HN culture. Furthermore. the PAL activities were detected in both of LC-MN and LC-HN cultures during a short period after the mycelial growth reached the peak. However, in HC-LN culture, PAL activity was detected before the mycelial growth peaked and maintained for another 6 days at higher level.

1995-P10

PEG に結合させたリグニンモデル化合物の白色腐朽菌及びその酵素による分解

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Fungal and enzymic oxidation of PEG-linked lignin model compound

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Abstract: We prepared a lignin model in which β-O-4 dimers were covalently attached to 8000 MW polyethylene glycol (PEG). The PEG-linked model was mineralized extensively in liquid medium and in solid wood cultures of the white-rot fungus *Phanerochaete chrysosporium*. GPC showed that *P. chrysosporium* degraded the PEG-linked model by cleaving its lignin dimer substructure rather than its PEG moiety. Cα-Cβcleavage was the major fate of the PEG-linked model after incubation with *P. chrysosporium* and also after oxidation with its lignin peroxidase. The brown-rot fungus *Gloeophyllum trabeum* was unable to degrade the PEG-linked model efficiently.

1995-P11

白色腐朽菌カワラタケのシュウ酸合成酵素の部分精製

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Partial purification of glyoxylate oxidase from the white-rot basidiomycete *Coriolus versicolor*

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Abstract: The glyoxylate oxidase which catalyses oxidation of glyoxylate to form oxalate was partially purified from the homogenate of a white-rot basidiomycete *Coriolus versicolor* .The g!yoxylate oxidase was purified by combination of (NH4)2SO4 precipitation. DEAE-Biogel A chromatography and Sephadex G-l50 gel filtration. Three isozymes were detected by DEAE-Biogel A chromatography.

1995-P12

白色腐朽菌 *Phanerochaete chrysosporium* の核酸要求性変異株の単離とその相補遺伝子の取得

中村雅哉、西田篤実、高野麻理子

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Isolation of uracil auxotrophic mutants from *Phanerochaete chrysosporium*

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Forestry and Forest Products Reserach Institute

Abstract: Uracil auxotrophic mutants of the white-rot fungus *Phanerochaete chrysosporium* using a positive screening procedure with 5-fluoro orotic acid. Mutants deficient for the orotidin-5'- phosphate decarboxylase (*pyr 4* mutants) and for the orotate phosphoribosyl transferase (*pyr 2* mutants) have been characterized by enzyme assays. The *pyr 4* gene was screened from a *P. chrysosporium* genomic library using the *Aspegillus nidulans pyr 4* gene as a probe. The *pyr 2* gene was amplifyed from *P. chrysosporium* genomic DNA by PCR using the *pyr 2* specific primers.

1995-P13

クラフト蒸解条件の酸素酸化漂白への影響 —蒸解条件による酸素酸化したパルプ中残留リグニンの構造変化

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Effect of kraft cooking conditions on effciency of oxygen delignification, -The structure characteristics of residual lignin in the oxygen delignified pulp

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1995-P14

リグニンスルホン酸添加バクテリアセルロース製造における菌株、炭素源の選択

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Selection of strain of *Acetobacter xylinum* and carbon source in cultuer medium with lignosulufonate for production of bacterial cellulose.

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Abstract: We have found that the cellulose yields of seven different strains of *Acetobactor xylinum* increased by the addition of lignoslufonate from sulfite pulping waste 2% glucose medium. In this study, we studied whether cellulose yield of each strain could be increased or not with different carbon source with or without lignosulfonte. We used Fructose, Glyserol, Saccharose, Xlose and Lactic acid as carbon source. The results indicated that cellulose yields of each strain of *A. xylinum* are not always increased by the use of different carbon source. The selections of strain and carbon source are very important to secure the cellulose yield.

1995-P15

熱分解ガスクロマトグラフィーによる広葉樹型リグニンの分析（III）—クラフト蒸解およびパルプ漂白による熱分解物の変化—

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Analysis of hardwood lignin by pyrolysis-gas chromatography (III), — Changes of pyrolysis products by kraft cooking and pulp bleaching —

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Abstract: Several Japanese hardwood kraft pulps were analyzed by pyrolysis combined with gas chromatography (Py-GC). The major pyrolysis products were guaiacol, 4-methylguaiacol, 4-vinylguiaicol, *trans*-isoeugenol, coniferylaldehyde, syringol, 4-methylsyringol, 4-vinylsyringol, trans-4-propenylsyrjngol, sinapaldehyde. The ratios of syringyl-derived pyrolysis products to guaiacyl-derived pyrolysis products were decreased by kraft cooking. The yields of pyrolysis products from lignin in chlorinated kraft pulp were small, and the chlorinated-derived pyrolysis products were rarely detected.

1995-P16

ケナフ靭皮部の酸素パルプ化

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Oxygen pulping of kenaf bast

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Abstract: Oxygen pulping of kenaf bast was carried out with 10%-20% NaOH of o.d. bast at 110 ºC and 7 kg/cm^2 of' O2 pressure for 60-120 min. Products were separated into pulp-1 (long fiber pulp), pulp-2 (screened pulp), fines (epidermis part) and a reaction liquor. After boiling with 50-70% AcOH, pulp-1 was further delignified and yielded the bast pulp. Satisfactory bast pulps with much greater delignification and physical properties were obtained in yields of 48%-56% when bast was subjected to oxygen pulping with 15% NaOH for 60-120 min, followed by boiling in aqueous AcOH. The reaction liquor was separated into three main fractions according to the fractional precipitate procedure and so on in order to analyze chemical properties and utilize as raw materials for biomass conversion.

1995-P17

酢酸リグニンを原料とする炭素繊維の調製（5）—針葉樹酢酸リグニンの炭素繊維化—

久保智史、石川直哉、浦木康光、佐野嘉拓

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Preparation of carbon fiber from acetic acid lignin (V), — Preparation of carbon fiber from softwood acetin acid lignin —

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Abstract: Preparation of lignin fiber as precursors for carbon fibers from softwood acetic acid lignin (NAL) was obtained from todomatu wood (*Abies sacahlininsis*) by aqueous AcOH pulping with 0.1% HCl at atmospheric pressure. NAL was infusible, though birch acetic acid lignin (BAL) was readily fusible without any chemical modification. However, F-2 which was precipitated from waste liquor by 70% aqueous AcOH and was obtained in a yield of 81% based on NAL, had fusibility and spinnability. Preparation of lignin fiber was achieved without thermal treatment, though the fiber had a rough surface and mechanical properties inferior to those for BAL fibers. F-2 was possible to undergo direct carbonization without thermal stabilization. Carbon fibers prepared from the lignin fibers of F-2 had worse mechanical properties compared with those for BAL fibers. The charactization of F-2 lignin fibers and carbon fibers seemed to be improved by addition of plasticizer for F-2 to have a lower fusible temperature for our handmade spinning apparatus.

1995-P18

Flavan-3,4-carbonate の開環重合による高重合度縮合型タンニンの合成とその機能

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Synthesis of high-molecular-weight condensed tannin by cationic ring-opening polymerization of flavan-3,4-carbonate and their function

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Abstract: In order to obtain high-molecular-weight condensed tannin, we synthesized newly flavan-3,4-carbonate and tried its cationic ring-opening polymerization with BF3-Et2O in CH2Cl2 at 0 ºC. The molecular-weight of polymers increased with an increase of reaction time, and the number-average degrees of polymerization (DPn) reached 47 after 264h. The protein-precipitating capacity was found to increase with an increase in the molecular weight of condensed tannin.

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1996-101

樹木の細胞壁リグニン生合成過程の免疫組織学的研究

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Immunohistochemistry of biosynthesis of lignin in woody plants

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Abstract: As protoxylem and mataxylern of angiosperms maturate and develop, the elements with more extensive secondary thickenings than that represented by a helix deposit the secondary wall in two stages. First, a helical framework is built (first-order secondary wall). Then, additional secondary wall material is laid down as sheets or strands or both between the gyres of the helix (second-order secondary wall). In this study, we report the intergrading of tracheary elements using by immno- histochemistry. We prepared antiserum for irnmunohistochemical analysis. Antiserums were raised against PAL, OMT, CAD, 4CL, and POX. The peptide in the expression vector pQE (QUIAGEN, Chatsworth, CA, USA) was expressed in *E. coli* cells. The ability of the antiserum to react with crude and purified protein from *P. kitakamiensis* was tested by Western immunoblotting. PAL OMT, CAD, 4CL and POX were localized specifically in cells of xylem, but not observed in parenchyma.

1996-102

樹木の桂皮酸 4-水酸化酵素遺伝子の発現様式の解析

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Expression analysis of a cinnamic acid 4-hydroxylase gene from a hybrid aspen, *Populus kitakamiensis*

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Abstract: In higher plants, Cinnamic acid 4-hydroxylose (CA4H) is the second enzyme involved in phenylpropanoid biosynthesis and is a member of cytochrome P-450 superfamily. Three CA4H genes, -*cyp73a*, *cyp73b*, Cnd *cyp73c*-, and a cDNA clone of *cyp73a* were isolated from a genomic library and a cDNA library of a hybrid aspen; *Populus kitakamiensis*, ctnd were characterized. They might be interrupted by two introns, respectively. *cyp73a* and *cyp73b* were very similar each other not only in coding regions but also in non-coding regions. Southern blot analysis showed that four homologous genes for CA4H constructed a small gene family in the diploid genome of *P. kitakamiensis.* In the promoter regions, there were many common *cis*-element-like sequences in phenylpropanoid biosynthesis genes. Here, we win report a tissue-specific expression manner of an aspen CA4H gene in transgeneic tobacco plants. We made a *cyp73a* promoter-GUS gene fused constract. It was introduced to tobacco and aspen cells. The GUS activity in transgenic tobacco plants with the *cyp73a* promoter-GUS fusion gene was mainly detected in the vasculor bundles and was strongly induced in a non-tisssue-specific manner by wounding.

1996-103

樹木細胞壁形成におけるリグニンと糖代謝遺伝子の特徴

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Characteristics of genes related to lignin and sugar metabolism in plant cell wall formation

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Abstract: Lignin biosynthesis and carbohydrate chain biosynthesis are closely related to cell wall formation of plant. We constructed the cDNA library from the one year old stem of *Populus kitakamiensis*, which showed active cell wall thickness and lignification. We isolated the cDNA fragments of Sucrose synthase, UGPase and DAHP synthase from the cDNA library. Sucrose synthase and UGPase are related to sugar

metabolism, and DAHP synthase is related to shikimic acid pathway and lignin biosynthesis. The nucleotide sequences and the deduced amino acid sequences of their DNA fragments showed that sucrose synthase and UGase of *P. kitakamiensis* are similar to other higher plant.

1996-104
シナピルアルコールを用いた広葉樹細胞壁木化過程シミュレーション
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Modeling of hardwood lignification using sinapyl alcohol
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Abstract: To be clear biosynthetic process and chemical structure of hardwood lignin, the effect of hydrophobicity of reaction media on dehydrogenative polymerization (DHP) of sinapyl alcohol was studied by using a horseradish peroxidase. First, to inhibit polymerization of sinapyl alcohol in water around the enzyme, the hydrophilic site of horseradish peroxidase was converted to be hydrophobic by modifying with methoxypolyethlene glycol succinimidyl succinate. Sinapyl alcohol was polymerized by the modified enzyme, and the products were analyzed by ^{1}H-NMR. Second, considering the lignification model that sinapyl alcohol is polymerized by β-O-4 linkage to syringaresinol formed previously, syringaresinol was used as starting radical at DHP process of sinapyl alcohol. Third, to examine the effect of hydrophobic media, polymerization of sinapyl alcohol in polysaccharide solution or hydrophobic solvents was investigated by ^{1}H-NMR. Further, structure of polymerized products of Cβ-labeled sinapyl alcohol (HO-C6H2(OCH3)2-CH=C＊H-CH2OH) was analyzed by ^{13}C-CP/MAS.

1996-105
広葉樹の CAD 形質転換体における異常リグニンの化学的構造について
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Chemical study on abnormal hardwood lignin with antisense cinnamyl alcohol dehydrogenase (CAD) gene
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Abstract: Various DHPs derived from mixtures or coniferyl aldehyde and sinapaldehyde with coniferyl and sinapyl alcohol were prepared for the model of the transgenic hardwood lignin. Fr-IR and UV analysis of the DHP showed that sinapaldehyde and sinapyl alcohol were effectively incorporated into these DHPs. However, GC-MS analyses of the thioacidolysis products of the DHPs showed that coniferyl aldehyde was significantly incorporated into the DHPs and end group via β-O-4 linkages, and the incorporation of sinapaldehyde into the DHPs as end group was very small. Therefore, the thioacidolysis products of sinapaldehyde were analyzed by GC-MS. The chromatogram gave a small peak of the extended product with relatively large amount of two new components derived from sinapaldehyde.

1996-106
カラスザンショウにおけるリグナン生合成
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Biosynthesis of lignans in *Zanthoxylum ailanthoides*
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Abstract: Interestingly *Zanthoxylum ailanthoides* have (8*S*,8'*S*)-furofran lignans such as (-)-pinoresinol and (8*R*,8'*R*)-(-)-secoisolariciresinol. It was suggested that insoluble residue from *Z. ailanthoides* catalyzed enentioselective (-)-pinoresinol formation from coniferyl alcohol. Incubation of cell-free extracts from the plants with (±)-pinoresinols in the presence of NAD(P)H resulted in the enantiospecific formation of (+)-lariciresinol, whose configuration was identical with that of natural (-)-secoisolariciresinol. Following administration of [8-^{14}C]coniferyl alcohol the radioactivities were incorporated in pinoresinol, lariciresinol and secoisolariciresinol with their (8*S*,8'*S*) enantiomer preferred. Following administration of [8,8'-^{14}C] pinoresinol, the formation of radioactive lariciresinol and secoisolariciresinol was found again, although they were almost racemic. These facts suggested the presence of both biosynthetic pathways to (8*S*,8'*S*) and (8*R*,8'*R)* lignans in the plant.

1996-107

トチュウのリグナン・ネオリグナンの生合成と立体化学

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Biosynthesis and stereochemistry of lignans and neolignans in *Eucommia ulmoides*

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Abstract: *Eucommia ulmoides* contains diverse lignans and neolignans. To investjgate their biosynthesis, [8-^{14}C]coniferyl alcohol was fed to excised young shoots, and it was incubated with cell-free extracts of the plant in the presence of H2O2 and with insoluble residue in the absence of cofactors. (+)-Pinoresinol formation was found in preference to the (-)-form in the feeding experiment. *Erythro*-isomer was more than the *threo* one in guaiacylglycerol-β-coniferyl ether obtained both in the feeding experiment and in the assay using the insoluble residue. (-)-Dehydrodiconiferyl arcohol and optically active *erythro* and *threo*-guaiacylglycerol-β-coniferyl ethers were formed in the assay using cell-free extracts in spite of their low enantiomeric excess (9-14%).

1996-108

Wikstroemia sikokiana から単離されたリグナンとその生合成経路について

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A possible biosynthetic pathway of lignans in *Wikstroemia sikokiana*

Tomoya Okunishi, Toshiaki Umezawa, Mikio Shimada

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Abstract: [9,9-^{2}H2OC^{2}H3]Coniferyl alcohol, [9,9,9’,9’-^{2}H4]pinoresinol, [9,9,9’,9’-^{2}H4]lariciresinol and [9,9,9’,9’-^{2}H4]]secoisolariciresinol were administered to *Wikstroemia sikokiana*, and incorporation of deuterium atoms into several lignans were observed. Based on the result, a possible biosynthetic pathway of lignans in *W. sikokiana* was proposed.

1996-109

Eucalyptus camaldulensis および *E. globulus* 各 2 個体の樹幹内変異を用いたリグニンの S／G 比とリグニン含有率の関係について

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Relationship between lignin content and lignin S/G ratio in the same trunk sought by their within-tree variations in *Eucalyptus camaldulensis* and *E. globules*

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Abstract: The relationship between extractives-free (EF) lignin content and lignin monomeric composition as syringyl/guaiacyl (S/G) ratio by thioacidolysis was examined. This was performed in the same trunk by their within-tree variations, which mean the investigation with the same genes, in *Eucalyptus camaldulensis* and *E. globules*.. As results, each species had a high negative correlation between EF-lignin content and lignin S/G ratio although the difference between species and/or individuals was observed in the trend of within-tree variations of the wood properties. The relationship between EF-lignin content and lignin S/G ratio is considered to be caused from the difference in the fiber morphology from the relationship between lignin and EF-basic density which may relate to the fiber morphology.

1996-110

5-Hydroxyguaiacyl nuclei in native lignin

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1996-111

多糖類存在下におけるリグニンモデル物質の反応

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Reaction of lignin model compounds in the presence of polysaccharides

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Abstract: The lignin model compounds of β-O-4 type were treated in dioxane and water (1:1) mixture at l80ºC for 20 min with and without spruce holocellulose. A model, guaiacylglycerol-β-guaiacyl ether (1) gave β-l (8), β-5 (9), β-β(10) dilignols and a trilignol (11) which are the products of recoupled radicals from homolysis of the model (1). However, when treated in the presence of holocellulose, these dimeric and trimeric compounds could not be detected. The results indicate that the polysaccharides act as hydrogen donor to stabilize the formed radicals before their coupling. The same results were also recognized in the case of otherβ-O-4 model compounds.

1996-112

分析的熱分析によるリグニンの分析　―熱分解生成物の起源構造について―

和泉明子、黒田健一

筑波大学農林工学系

Analytical pyrolysis of lignin : origins of pyrolysis products

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Abstract: Lignin model compounds, β-β and β-5 types, were pyrolyzed in the presence of tetramethylammonium hydroxide (TMAH) to obtain information on the lignin structure. Pinoresinol and syringaresinol yielded full methylated products as main products. The full methylated product (M^+ 400) of dehydrodiconiferyl alcohol was not observed. However, dehydrodiconiferyl alcohol showed the formation of three methylated products, which were isomers from their mass fragment patterns (M^+ 370). These methylated dimer products were also observed in the pyrolysis of hardwood type dehydrogenative polymers.

1996-113

熱分解-メチル化によるリグニンの分析：β-O-4 型構造由来の熱分解生成物

黒田健一

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Pyrolysis-gas chromatography analysis of lignin in the presence of tetra-methylammoniurn hydroxide: β-O-4 substructure-derived pyrolysis products

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Abstract: To obtain pyrolysis fragments with information on the lignin structure, a dehydrogenation polymer of coniferyl alcohol was pyrolyzed in the presence of tetramethylammonium hydroxide (TMAH) at 500 ºC for 4 s. A series of methylated products were swept on a gas chromatograph column. The products, such as (3,4-dimethoxyphenyl) methoxyethylenes and 1-(3,4-dimethoxy- phenyl)-1,2,3-trimethoxypropanes, derived from the β-O-4 building blocks were observed in the pyrolyzate. TMAH/pyrolysis of Japanese cedar and Japanese Douglas fir woods also produced these products. The sources of some products were explained on the basis of the TMAH/pyrolysis results of β-O-4 type lignin model compounds. Abundances of the β-O-4 building blocks in lignin were compared among the woods and several isolated lignins using the peak intensities of 1-(3,4- dimethoxyphenyl)-1,2,3-trimethoxypropanes. Results showed that TMAH/pyrolysis offers much information on the β-O-4 1ignin building blocks than conventional pyrolysis without TMAH.

1996-114

リグニンの β-O-4 構造の化学反応牲（2）―ルイス酸触媒アセトリシスによるリグニンの β-O-4 構造の定量―

小幡雅子、中坪文明

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Chemical reactivity of β-O-4 substructures in lignins, -Quantitative analysis of β-O-4 structures in lignins by Lewis acid catalyzed acetolysis (LCA) -

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Abstract: In our recent investigation, Lewis acid catalyzed acetolysis (LCA) reaction has been shown to be a suitable degradation method for the analysis of β-O-4 substructures in lignins, for its characteristic reactivity and the simple experimental procedure. Here, we describe the synthesis of Hibbert's ketones in order to identify the degradation products, and discuss some structural aspects of *Eucalyptus globules* MWL from its LCA reaction products.

1996-115

機械パルプの光褪色におよぼすフェノール性水酸基の影響

足立幸雄、伊藤和貴、坪田弘志、沖 妙、橘 燦郎
愛媛大学農学部

Effect of phenolic hydroxyl groups in mechanical pulps on depression of color reversion of mechanical pulps

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Faculty of Agriculture, Ehime University

Abstract: In order to investigate the effect of phenolic hydroxyl groups in mechanical pulps on depression or light-induced color reversion of mechanical pulp, two types or mechanical pulp (thermomechanical pulp : TMP, groundwood pulp : GP) were acetylated, and examined to what extent the color reversion of the pulps was prevented by the acetylation. When about 11% of the phenolic hydroxy groups in unbleached GP and unbleached TMP were acetylated, the color reversion or the pulps were also completely depressed. On the other hand, when about 16% and 29% of the phenolic hydroxy groups in bleached GP and bleached TMP, respectively, were acetylated, the color reversion of the pulps were completely depressed. On the basis of these results, the phenolic hydroxyl groups in mechanical pulps seem to contribute mainly to the depression of the color reversion of mechanical pulps.

1996-116

バクテリアセルロース製造培地における緩衝液成分およびリグニンスルホン酸の役割

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Role of buffer components and lignosulfonate in the superior medium for bacterial cellulose production

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Faculty of Agriculture, Kochi University

Abstract: We have already reported bacterial cellulose membrane yield is greatly increased by the addition of lignosulfonate to a standard cultivation medium. In this report we examined the relationship between concentration of buffer, yield of cellulose membrane and final pH of media to clarify the role of buffer components and lignosulfonate in the superior bacterial cellulose production medium. The results showed that the final pH values of media with lignosulfonate were slightly higher than those media without lignosulfonate but the cellulose yield increases were greater. Only citric acid was probed to be the effective component for the superior cellulose production system with lignosulfonate.

1996-特別講演

樹木系フェノールポリマーとエコテクノロジー

阿部 勲
三重大学生物資源学部

Woody phenolpolymers and ecotechnology

Isao Abe
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Abstract: The investigations on woody phenolpolymers, namely wood lignin and some bark proanthocyanidins (condensed tannins) I participated were summarized, and the forest ecotechnology concerning the specific species, which contained highly of condensed tannins in bark, was discussed.

1996-201

オイルパーム・フロンド爆砕パルプからのボードの調製と爆砕パルプ中のリグニンの性状

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Preparation of binderless boards from steam exploded pulp of oil palm frond and structural characteristic of lignin in steam exploded pulp

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Abstract: The binderless boards were prepared from steam exploded (2.0-3.0MPa, 5-10min) pulps of oil palm frond. The strength of these boards met the requirements of the boards of JIS. To clarify the mechanism of the bonding of the binderless boards, oil palm frond, pulp and board were analyzed by the chemical and spectrometical methods and pyrolysis-gas chromatography mass spectrometry. Björkman lignin from oil palm frond, and this lignin was characterized by the presence of significant amount of esterified *p*-hydroxybenzoic acid. Most ester bonds and β-*O*-4 bonds were cleaved during steam explosion process, and the other hand, guaiacyl units were condensed greatly, as revealed by ^{1}H and ^{13}C-NMR spectra, Moreover, the structural difference of the aromatic units between 2.5MPa and 3.0MPa exploded pulp, were observed in ^{1}H, ^{13}C-NMR and FTIR spectra. The ratios of syringyl derivatives to guaiacyl derivatives (S/G) from total ion pyrograms were decreased by hot pressing. As a result of the analytical pyrolysis, 5-hydroxymethylfurfural, derived from cellulose, was increased by the steam explosion especially 3.0MPa. Significant amount of furfural, derived from pentosan, was detected in the pulp steam exploded under the condition of 2.5MPa, and furfural was increased during hot pressing. These facts suggest that furfural is involved in the formation of binder together with lignin.

1996-202

蒸解黒液中のリグニンの性状に関する研究

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日本製紙株式会社

Studies on lignin in the kraft black liquor

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Abstract: We analyzed a black liquor to establish a method to determine a pulp yield. When the black liquor was acidified to separate lignin and other wood components, it was observed that kraft cooking with anthraquinone (AQ) increased the rate of precipitated lignin to the total lignin in the black liquor. Determinations of functional groups of precipitated lignin, "kraft lignin", and acid- soluble lignin, indicated that AQ did not give a significant influence to a character of kraft lignin, but did much to one of acid-soluble lignin. It would be suggested that AQ decreased the acid-solubility of lignin by preventing formation of lignin-carbohydrates-complex (LCC) containing carboxylic acids derived from carbohydrates degradation compounds.

1996-203

酸素−アルカリ漂白過程における多糖類の分解機構（6）—過酸化物の安定性と炭水化物分解の関連について—

横山朝哉、松本雄二、飯塚堯介
東京大学大学院農学生命科学研究科

Degradation mechanisms of carbohydrate during oxygen-alkali bleaching (VI), — Relationships between peroxide stability and carbohydra te degradation —

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Abstract: A cellulose model compound, methyl β-D-glucopyranoside (MGP), was treated with an alkaline hydrogen peroxide solution in the presence or absence of metal ions, such as iron, manganese and magnesium, and the effect of these metal ions on the degradation of MGP was examined. The results showed that the amount of degraded MGP at a certain consumption of hydrogen peroxide was strongly dependent on the metal ions. The addition of iron did not cause more MGP degradation than the case of no metal addition, and the less MGP degradation was observed when more magnesium was added together with iron. Contrarily, the addition of manganese caused only a little degradation of MGP though the rate of hydrogen peroxide degradation was very high, and the addition of magnesium together with manganese had no positive effect on the protection of MGP. The sole addition of magnesium had some positive effect on the protection of MGP but the complete protection of MGP was not obtained.

1996-204
リグニンおよび兼モデル化合物とオゾンとの直接の反応によるヒドロキシラジカルの生成
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Martin Ragnar[*1], Tord Eriksson[*1], Torbjörn Reitberger[*2]
Formation of hydroxyl radicals from direct ozone reactions with lignin and carbohydrate model compounds —A kinetic study
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Abstract: オゾンがリグニンモデル化合物と反応する際には、二重結合を酸化的に解裂する通常のイオン的な酸化反応のほかに、一電子的にフェノールを酸化してフエノキシラジカルを生成するラジカル的な反応が考えられる。その時に生じるオゾンの還元生成物は酸素とヒドロキシラジカルに分解するので、オゾン漂白中の多糖類分解の原因となることを明らかにした。このラジカル的な酸化反応の反応速度は、反応の相手方であるフェノールの酸化電位と直線的な相関を示す。反応 pH が高いと反応速度は急激に増大する。

1996-205
化学パルプの高収率化と無塩素漂白に関する研究、亜硝酸処理におけるリグニンの反応
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Pretreatment for chemical pulping and non-chlorine bleaching reactions of lignin during nitrous acid treatment
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Abstract: Nitrous acid treatment of kraft pulp has been proposed as a non-chlorine bleaching method. This treatment is also expected to be effective as a pretreatment for kraft pulping to increase the pulp yields. Behaviors of lignin degradation during the nitrous acid treatment were studied using beech wood meals and nonphenolic β-*O*-4 type lignin model compounds. The delignification during kraft pulping was accelerated by the pretreatment. By the nitrous acid treatment, veratrylglycerol-β-syringyl ether (VS) and α-ethyl ether of VS (VSE) were distinctly degraded through cleavage of their Cα-Cβbonds giving veratraldehyde in a 51 and 47 mol% yields, respectively. Both erythro and threo of the lignin models were treated with nitric acid solution in the absence and presence of nitrite, and the degradation behaviors were discussed.

1996-206
白色腐朽菌によるポリエチレンの生分解（I）
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Polyethylene biodegradation by white rot fungi
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Abstract: Polyethylene (PE) biodegradation by white rot fungi, IZU-154, *Phanerochaete chrysosporium*, and *Trametes versocolor*, was investigated. PE was effectively biodegraded under the nutritional nitrogen- and/or carbon-limited culture condition, and IZU-154 showed the most significant PE biodeqadation among three white rot fungi. The addition of manganese sulfate into nitrogen- and/or carbon-limited medium enhanced the PE biodegradability of white rot fungi. These results suggest that manganese peroxidase (MnP) plays a significant role in the PE biodegaradation by white rot fungi, and *in vitro* PE biodegradation by isolated MnP supports this hypothesis.

1996-207
リグニン生分解に関する研究（VII) ～バイオブリーチングにおける針葉樹クラフトパルプ残留リグニンの構造変化～
片桐誠之、堤　祐司、西田友昭
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Studies on lignin biodegradation (VI), Changes in the residual lignin framework in softwood kraft pulp during biobleaching by *Phanerochaete chrysosporium* and manganese peroxidase

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Abstract: Softwood kraft pulp (SWKP) was treated with *Phanerochaete chrysosporium* or with its manganese peroxidase (MnP) under both conditions of which Mn(II) was added or not, and the residual lignin frameworks were compared among these treated pulps by the chemical analysis (nitrobenzene oxidation, acidolysis and permanganate oxidation). In the treatment of SWKP by *P. chrysosporium* without Mn(II) addition, the residual lignin was degraded and selective decrease of arylglycerol-β-aryl ether unit was observed. On the other hand, the treatment of SWKP with partially purified MnP without Mn(II) addition revealed that MnP can not degrade the residual lignin because of lack of manganese in SWKP. These results suggested that enzyme(s) other than MnP may contribute to delignification of SWKP by *P. chrysosporium* under manganese-insufficient condition.

1996-208

白色腐朽菌のリグニン分解に関与する酵素系に関する研究 (X) ～*Phanerochaete sordida* YK−624 株の産生する NAD(P)H 依存性 Fe(III)還元酵素について～

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Studies on ligninolytic enzymes of white-rot fungi (X), NAD(P)H-dependent ferrireductase produced by *Phanerochaete sordida* YK-624

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Abstract: We have previously reported NAD(P)H-dependent reduction of manganese dioxide mediated by ferrous chelate in white-rot fungus *Phanerochaete sordida* YK-624. In the present study, we tried to isolate ferrireductase which would involve in the reduction or manganese dioxide by *P. sordida* YK-624. Ferrireductase activity was detected in cell-free extract, and most of the ferrireductase was precipitated by the addition of 30-65% ammonium sulfate saturation. The ferrireductase was purified to homogeneity by hydrophobic, gel filtration, and Mono Q chromatography. This enzyme was monomer protein, and pI and molecular weight were 5.1 and 35 kDa, respectively. Optimal pH for the reduction of ferric chelate by this enzyme was about 7.0. This reductase was dependent on NADPH although cellobiose could not act as electron donor. In the kinetic analysts, this enzyme showed higher substrate specificity for ferric chelate than Mn(III) and lignin model compounds.

1996-209

Ganoderma sp. YK505 株の産生するマンガンペルオキシターゼの諸特性とクラフトパルプ漂白性

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Bleaching of kraft pulp with manganese peroxidase secreted from *Ganoderma* sp. YK-505 and properties of the enzyme

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Abstract: We performed *in vitro* bleaching of an unbleached hardwood kraft pulp (UKP) with manganese peroxidase (MnP) from the white rot fungus *Ganoderma* sp. YK-505 or *Phanerochaete sordida* YK-624. MnP from *Ganoderma* sp. YK-505 could brighten UKP at higher temperature and concentration of H2O2 than with MnP from *P. sordida* YK-624. Two MnP isoenzymes were purified from shaken culture of *Ganoderma* sp. YK-505. The molecular masses of both isoenzymes were about 43 kDa. Maximum activities of both isoenzymes were exhibited at 55ºC. Both isoenzymes had higher resistance to H2O2 and different pH dependency from other MnPs, e.g. MnP from *Phanerochaete chrysosporium* and *P. sordida*, and maintained activities at high pH (6-8.5).

1996-210

アルカリ耐性担子菌 *Phellinus* sp. IS-847 株が産生するフェノールオキシダーゼについて

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Characterization of phenoloxidases from anti-alkaline basidiomycete *Phellinus* sp. IS-847

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Abstract: Anti-alkaline basidiomycete *Phellinus* sp. IS-847 isolated from nature grew in an alkaline wood mill + buffer medium (pH 8) very well, and secreted exracellular phenol oxidases, which contained two isoenzymes. The main isoenzyme (PhO I) was isolated and purified by using hydrophobic, gel filtration and anion exchange chromatography. This isoenzyme had molecular mass of about 60 kDa and isoelectric point of about 6.3. The optimal pH was 6.0 when guaiacol was used as a substrate. The substrate specificities and the effect of inhibitors were similar to the behavior of known laccases. The minor isoenzyme (PhO II) had molecular mass of about 63 kDa and pI 4.8, and showed high activity in an alkaline region than PhO I did.

1996-211

木材腐朽菌 IO−427 株による難分解性 β-*O*-4 型リグニンモデル化合物のエーテル結合開裂について
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Cleavage of ether linkage in recalcitrant β-O-4 lignin model compound by wood-rot fungus IO-427
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Abstract: The β-ether linkage is the most abundant in chemical structure of lignin, therefore, it seems that the cleavage of this linkage is the most important process in the lignin biodegradation. From this viewpoint, we tried to isolate fungi which can release fluorescent 4-methylumbelliferone by the cleavage of the β-ether bond in Substrate I, which is recalcitrant β-*O*-4 type lignin model compound, 3-hydroxy-2-(4-methylumbelliferyl)-1-phenyl-l-propanone. By this screening method, we selected a wood-rotting fungus lO-427. In the present study, we tried to determine the metabolites from Substrate I in order to examine cleavage process of β-ether linkage. After 24 hour-incubation, Substrate l decreased by 23%, and 20% of 4-methylumbelliferone was produced. Two kinds of C6-C3 compounds were found, and they were identified as 2.3-dihydroxy-1-phenyl- 1-propanone, and 3-hydroxy-1-phenyl-1-propanone. These compounds and 4-methylumbelliferone weren’t detected in the culture of *Phanerochaete chrysosporium* although decrease of Substrate I was observed. It was expected that lO-427 might possess different function of the cleavage of β-*O*-4 linkage from other white-rot fungi.

1996-212

木材腐朽菌による LCC の分解について (VI)　DSC 分析によるリグニン—糖マトリツクスの変化の検出
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Degradation of lignin-carbohydrate complex by wood-rotting fungi (VI), Detection of changes of lignin-carbohydrate matrix by differential scanning calorimeter (DSC)
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Abstract: Differential scanning calorimetric (DSC) analysis was applied to the akamatsu LCC (Lignin-Carbohydrate Complex) degraded by wood-rotting fungi, a brown-rot fungus *Tyromyces palustris* and a white-rot fungus *Coriolus versicolor*. Original LCC indicates two exothermal peaks at 440-470ºC and one shoulder at 330ºC. Comparing with the component materials prepared from akamatsu wood, the peak determined at 440-470ºC is considered to be due to the lignin- carbohydrate matrix. DSC analysis of degraded LCC indicated that *T. palustris* degraded only the carbohydrate portion in lignin-carbohydrate matrix and that *C. versicolor* decomposed the lignin portion to form the fragments with less lignin amount.

1996-213

針葉樹の常圧プロピレングリコールパルプ化
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Pulping of softwoods by propylene glycol system at atmospheric pressure
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Abstract: Organosolv pulping of softwoods was investigated in polyhydric alcohols containing mineral acids at atmospheric pressure. The propylene glycol (PG) pulping with sulfuric acid gave satisfactory pulps with little rejects and the very low content of residual lignin, which were readily bleached. Mechanical properties of the pulps were comparable to those of KP. The bleached pulp has considerably high glucose and α-cellulose contents, and high crystallinity that was further increased by simple chemical treatment. Therefore, the pulps are suggested to be utilized as not only paper but also dissolved pulp and highly crystalline cellulose. The pulping solvent is supplied from hydrolyzed hemicellulose, and the waste liquor including hemicellulose after removal of PG lignin can be re-used as the solvent. This suggests to reduce the cost of the pulping. Consequently, the PG pulping is considered an alternative process to conventional chemical pulping.

1996-211

ササ稈の触媒添加蒸煮処理

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Acid-catalyzed steaming treatment of bamboo grass, *Sasa senanensis* Rehd

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Abstract: The effect of acid catalysts in the steaming treatment on solubilization of bamboo grass xylan was investigated. Among catalysts used, FeCl3 and CaCl2 were efficient in solubilization of xylo-oligosaccharides at a level of 10 mmole/kg substrate and below. When the substrate was steamed in the presence of these catalysts at 191ºC for 10 min, xylo-oligosaccharides were obtained in a yield of 8-9% based on the raw material. The enzymatic digestibility of residual fiber was also determined. The catalysts were found to be effective on enhancement of the susceptibility to cellulase. Water extract of steamed bamboo grass showed inhibitory activity to the angiotensin I -converting enzyme (ACE). The lC50 value was 0.06 mg/ml.

1996-215

水蒸気圧縮処理による樹液抽出法の開発

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Development of sap extraction method associated with the compressive molding process

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Abstract: For the utilization method of forest resources, there is a gathering of sap for the particular purpose excepting the use of wood itself for building materials, pulp and paper. The purpose of this study was a development of sap extraction method associated with the compressive molding process of *Cryptomeria japonica* D.Don. and *Camaecypariss obutusa* Endl. for effective utilization of wood. In analysis of wood sap squeezed from *Cryptomeria japonica* during compressive molding process of raw wood with steam treatment, four compounds were isolated from the chloroform extraction and idendfied by ^{1}H-NMR and MS. These compounds were coniferyl alcohol, D,L-pinoresinol, lariciresinol and dihydrodehydrodiconiferyl alcohol. On the other hand, judging from the fact that two compounds, D,L-pinoresinol and dihydrodehydrodiconiferyl alcohol, were isolated from the hydrolyzed water layer, high amount of lignan-glycosides was contained in original sap.

From the *Camaecyparis obutusa* wood sap, hinokinin was isolated from the chloroform extraction and idendfied by NMR and MS.

1996-216

リグニンを原料とするポリウレタンの熱的及び粘弾性的特性

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Thermal and viscoelastic properties of polyurethanes from lignin

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Abstract: Polyurethane (PU) sheets were prepared from alcohol-solvolysis lignin (AL) and kraft lignin (KL) by the following procedures. Lignin and polyethylene glycol having a molecular weight of 400 (PEG 400) were dissolved in tetrahydrofuran (THF). Diphenyrmethane diisocyanale (MDI) was added to the above solution and the reaction was continued at room temperature until a prepolymer solution was obtained. The prepolymer solution was cast on a glass plale which was placed in a desiccator. After the removal of THF, the obtained prepolymer sheet was cured at 120 ºC for24 hr. The thermal and viscoelastic properties of PU's were studied by thermogravimetry (TG), differential scanning calorimetry (DSC). and dynamic thermomechanometry

(DMA). Thermal degradation temperatures (Td's) slightly decreased with increasing lignin contents in PU's. Glass transition temperatures increased with increasing lignin contents in PU's. A large peak was observed in a tan□ curve at the temperature region where E' showed a sudden decrease. It is considered that this peak can be attributed to the main chain motion of PU's.

1996-P01
熱分解ガスクロマトグラフィーによる南洋材リグニンの分析
大井　洋、安田有紀野、和泉明子、黒田健一
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Analysis of lignin in tropical hardwoods by pyrolysis-gas chromatography
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Abstract: Ratios of syringyl units to guaiacyl units (S/G ratios) of lignin in tropical hardwoods were estimated by pyrolysis-gas chromatography (Py-GC). The wood meals were extracted with benzene and successively with 70% acetone/ water to remove tannins and other phenols. The observed S/G ratios were in good agreement with syringaldehyde/vanilin (S/V) ratios obtained by nitrobenzene oxidation. Furthermore, the extracted kapur wood meals were treated with hot 1 % NaOH solution to extract lignin-like substances in a tropical wood. Both syringyl and guaiacyl pyrolysis products were obtained from a chloroform soluble part of the 1 % NaOH extractives. In order to simplify a method for determination of acid-insoluble (Klason) lignin in tropical hardwoods, wood samples were hydrolyzed at 121ºC, and the acid-insoluble residue was characterized by Py-GC.

1996-P02
シリンギル基又はグアイアシル基を持った化合物の酸化によって生成するフリーラジカル
鬼木隆幸、高浜有明夫
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Free radicals produced by oxidations of compounds containing syringyl or guaiacyl groups
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Kyushu Dental College

Abstract: Electron spin resonance spectra of free radicals produced by oxidations of compounds containing syringyl or guaiacyl group were measured at pH 13.0. Syringaldehyde or 2,6-dimethoxy-*p*-hydroquinone showed an ESR signal of 2,6-dimethoxy-*p*-benzo-semiquinone radical by the oxidation with H2O2. This radical was also produced by the oxidation of dioxane lignins with hexacyanoferrate (III) or H2O2. Vanillin or methoxy-*p*-hydroquinone showed an ESR signal due to methoxy-*p*-benzosemiquinone radical by the oxidation with H2O2. A radical produced by the oxidation of methoxy-*p*-hydroquinone with O2 or hexacyanoferrate (III) was also observed when dioxane lignin was oxidized with O2 or hexacyanoferrate (III). Two kinds of radicals which were observed in the oxidation of dioxane lignins were identified to be due to syringyl and guaiacyl groups in the lignins.

1996-P03
フエノキシラジカルと酸素との反応性
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Reactivity of phenoxyl radical with molecular oxygen
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Abstract: The possibility of the reaction between phenoxyl radical and molecular oxygen was examined. Vanillyl alcohol (VA) or syringyl alcohol (SA) was treated with a one electron oxidizing reagent, manganese (III), and the effect of oxygen pressure on the yield of methanol from these phenols was determined. Methanol can be released when the radical produced at the carbon to which a methoxyl group is attached combines either with phenoxyl radical or with molecular oxygen. Although methanol was produced from a reaction under nitrogen pressure (oxygen 0 MPa), the increased yield of methanol under increased oxygen pressure was thought to indicate the reaction between phenoxyl radical and molecular oxygen.

1996-P04

酸素−アルカリ漂白過程における多糖類の分解機構(7)—リグニンの酸素酸化反応の速度論的特徴—

松本雄二、横山朝哉、飯塚堯介
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Degradation mechanism of carbohydrate during oxygen-alkali bleaching(VII), Kinetic behavior of lignin during oxygen oxidation in aqueous alkali solution

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Abstract: Isolated kraft lignin was treated with oxygen-alkali and the extent of oxygen oxidation was evaluated on the basis of the consumption of permanganate by the kraft lignin before and after the oxygen oxidation. One unit of kraft lignin (200 g) was found to be oxidized by 8.5 mole electron during oxygen-alkali treatment. Kinetic analysis showed that the process of oxygen oxidation can mainly be divided into two first order reactions. An acceleration of oxidation during the reaction, which was observed when model phenols were treated by oxygen-alkali, was not observed.

1996-P05

Thuya 属のリグナン生合成について

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Lignan biosynthesis of *Thuja* species

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Abstract: In addition to the previously found 2-(3,5-dimethoxy-4-hydroxybenzyl)-3-(3,4-methylendioxy-benzyl)-butyrolactone (4-*O*-demethylyatein), three lignans, secoisolariciresinol, matairesinol and dihydrodehydrodiconiferyl alcohol as minor components were confirmed in young shoots and leaves of *Thuja occidentalis*. Next, to investigate biosynthesis of lignans in Thuja species. [9,9-^{2}H2,O^{2}H3]coniferyl alcohol was fed to excised young shoots of *T. occidentalis* and *T. plicata*.

Following metabolism for 24 hr, deuterated pinoresinol, lariciresinol and dihydrodehydrodiconiferyl alcohol were formed in *T. occidentalis* young shoots. Cell-fee extracts from *T. occidentalis* leaves catalyzed the formation or deuterated pinoresinol, when incubated with [9,9-^{2}H2,O^{2}H3]coniferyl alcohol in the presence of NADPH and H2O2.

1996-P06

植物培養細胞によるフェノール類のグルコシル化の試み

村中俊夫、伊藤和貴、沖 妙、橘 燦郎
愛媛大学農学部

Trial for glucosylation of phenols by plant cell cultures

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Faculty of Agriculture, Ehime University

Abstract: Production of phenolic glucosides from three phenols, salicyl alcohol, coniferyl alcohol and coniferyl aldehyde by cell suspension cultures of *Coffea arabica* was tried. From the results of HPLC analysis of each reaction product, we found that salicin, phenolic glucoside of salicyl alcohol was produced in the maximum yield of 17.5% by the cultures of *C. arabica*. However, the glucosides from the two other phenols could not be produced by the cultures of *C. arabica*.

1996-P07

カワラタケラッカーゼ遺伝子の解析

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Analysis of laccase genes from *Coriolus versicolor*

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Abstract: Eight chromosomal DNA bands of *Coriolus versicolor* have been resolved by pulsed-field gel

electrophoretic analysis. The estimated sizes of the chromosomal DNAs ranged from 5.6 to 2.5 megabase pairs. Previously, we cloned and sequenced Laccase III gene (*CVL3*) and other laccase gene(*CVLG1*) of *C. versicolor*. The membrane, which was transferred the separated chromosomal DNAs of *C. versicolor*, was hybridized with gene specific probes of *CVL3* and *CVLG1*. It is cleared that *CVL3* and *CVLG1* were different chromosomal DNAs.

1996-P08
担子菌 *Coriolus versicolor*（カワラタケ）のフェノールオキシダーゼ遺伝子のクローニング
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資源環境技術総合研究所
Cloning and sequencing of a phenoloxidase gene from the basidiomycete *Coriolus versicolor*
Yosuke Iimura, Kenji Tatsumi
National Institute for Resources and Environment

Abstract: The gene (*cvmnp*) encoding a manganese peroxidase from *Coriolus versicolor* IFO 30340, a lignin-degrading basidiomycete, was cloned and sequenced, and the corresponding *cvmnp*, cDNA was also cloned and sequenced. The isolated gene consist of 1,397 bp, with the coding sequence being interrupted by 5 introns and flanked by an upstream region in which putative TATA and inverted CCAAT consensus sequences could be identified at positions -81 and -162, respectively. A potential metal responce element (MRE), xenobiotic responce element (XRE), and nitrogen regulatory consensus sequence (NIT) are recognized in the upstream region of the gene. The mature translation product, preceed by a 26-residue signal peptide, should consist of 339 residues.

1996-P09
白色腐朽菌 *Pleurotus ostreatus* のフルトラニル耐性変異株におけるコハク酸デヒドロゲナーゼ Ip サブユニット遺伝子の解析
松山拓郎、入江俊一、本田与一、渡辺隆司、桑原正章
京都大学木質科学研究所
Analysis of the genes encoding succinate dehydrogenase lp subunit from flutolanil-resistant mutant *Pleurotus ostreatus* strains
Takuro Matsuyama, Toshikazu Irie, Yoichi Honda, Takashi Watanabe, Masaaki Kuwahara
Wood Research Institute, Kyoto University

Abstract: For development of an useful vecter system in basidiomycetes, it is desired to develop a dominant genetic marker which requires no genetic background of the host strains. We have obtained several mutant *P. ostreatus* strains resistant to a carboxin-derived fungicide, flutolanil, from UV irradiated basidiospores of wild-type strains. We examined to clone a gene encoding succinate dehydrogenase iron-sulfer (Sdh lp) subunit, *Sdi*, which is thought to be concerned with the flutolanil resistance, using PCR technologies. And we tried to determine the nucleotide sequence of the gene from wild-type and mutant strains. As a result, total sequence of wild-type *Sdi* has been determined, and those of mutant strains are currently being analyzed.

1996-P10
天然からのダイオキシン分解能を有する分解菌のスクリーニング
大川浩樹、平林達也、伊藤和貴、沖　妙、橘　燦郎
愛媛大学農学部
Screening of fungi having ability for degradation of dioxins
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Faculty of Agriculture, Ehime University

Abstract: The time-course of the activities of lignin peroxidase, manganase peroxidase and laccase from the six fungi having ability for degradation of 2.7-Dichlorodibenzo-*p*-dioxin (2,7-DCDD) isolated by the screening method was measured in connection with the degradation rate of 2,7-DCDD. Correlation between the activity of lignin peroxidase and the degradation rate of 2.7-DCDD was observed. However, the activities of manganese peroxidase and laccase were not correlated to the degradation rate of 2.7-DCDD. From the results obtained above, we tried to modify the screening method found previously.

1996-P11
白色腐朽菌 WD544 菌株による色素の分解について

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Degradation of dyes by white-rot fungus WD544 strain
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Forestry and Forest Products Research Institute

Abstract: Four dyes decolorization plates tests using RBBR, PolyR, Poly S and Azure B were conducted with 26 wood-rotting fungi. WD544 was the only strain that decolorized all of 4 dyes on the test plates containing High-C, Low-N medium. WD544 decolorized RBBR and Poly R not only on the H-C, L-N plates while Poly S and Azure B were decolorized only under H-C, L-N condition. RBBR was also decolorized in both shaken and stationary liquid cultures, but the other 3 dyes were decolorized only under static conditions. Laccase activity was assayed during stationary cultivation but lignin peroxidase activity was rarely observed in these cultures. Time course change in visible

spectrum of each of 4 dyes suggested that RBBR was degraded in the liquid culture and the other 3 dyes were removed predominantly by fungal adsorption and further degraded on or in the mycelium.

1996-P12
ケナフ化学成分の総合利用 —靭皮部と本部のパルプ化—
敖日格勒、佐野嘉拓、浦木康光
北海道大学農学部
Utilization of kenaf component. -Pulping of bast and wood-
Aorigele, Yoshihiro Sano, Yasumitsu Uraki
Faculty of Agriculture, Hokkaido University

Abstract: Oxygen pulping of kenaf bast was carried out with 150% NaOH of o.d. bast at 110ºC and 7 kg/cm^2 of O2 for 90 min. After boiling with 70% AcOH, bast pulps with much great delignification and satisfactory physical properties were obtained in yields of 48%. The pulp was easily bleached at 85% brightness by ECF bleaching. For the total utilization of kenaf stalk kenaf wood (core) and stalk (core and bast) were pulped by solvent systems using aqueous AcOH with mineral acids at refluxing temperature and aqueous EtOH with AcOH at l70.

1996-P13
リグニン生分解に関する研究（VIII）—マンガンペルオキシダーゼによる針葉樹クラフトパルプの濃色化—
江原克信、堤 祐司、西田友昭
静岡大学農学部
Studio a on lignin biodegradation (VIII), The darkening of softwood kraft pulp with manganese peroxidase
Katunobu Ehara, Yuji Tsutsumi, Tomoaki Nishida
Faculty of Agriculture, Shizuoka University

Abstract: The brightening performance of softwood haft pulp (SWKP) during manganese peroidase (MnP) treatment and the yields of alkaline nitrobenzene oxidation products from the treated pulp were compared to clarify the mechanism of darkening of SWKP by MnP treatment. The yields of oxidation products markedly decreased with the brightness started to decrease, and the yields kept same level after when the pulp brightness increase thereafter. On the other hand, the yields from untreated hardwood kraft pulp (HWKP) were much less than that from SWKP and kept the same level during the brightness increase by MnP treatment. These results suggest that non-condensed type lignin may he oxidatively condensed and lead to the darkening of SWKP during MnP treatment.

1996-P14
β-O-4 型 LCC モデル化合物のリグニンペルオキシダーゼによる分解
宮田 聡、梅澤俊明、服部武文、島田幹夫
京都大学木質科学研究所
The degradation of β-*O*-4 type lignin carbohydrate complex model compounds by lignin peroxidase
Satoshi Miyata, Toshiaki Umezawa, Takefumi Hattori, Mikio Shimada
Wood Research Institute, Kyoto University

Abstract: Nonphenolic β-*O*-4 type lignin carbohydrate complex model compounds (LCCs) as well as the corresponding β-*O*-4 dimers were degraded by lignin peroxidase (LiP), and time course of oxidation of the substrates and product formation was monitored. No significant differences in the LiP catalyzed oxidation were

observed between the LCC model compounds and the β-*O*-4 dimers. The result indicated that the sugar moiety of the LCC model compounds did not prevent, at least qualitatively, oxidation of the LCC model compounds by LiP.

1996-P15

白色腐朽菌のリグニン分解に関与する酵素系に関する研究（XI）～クラフトパルプのバイオブリーチングにおけるパルプ中のマンガンイオンの状態変化～

平井浩文[*1]、近藤隆一郎[*1]、坂井克己[*1]、鬼木隆幸[*2]
[*1] 九州大学農学部、[*2] 九州歯科大学一般教育部

Studies on ligninolytic enzymes of white-rot fungi (XI), Change of oxidation number of manganese in kraft pulp during biological bleaching

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Abstract: The oxidation number of manganese in unbleached hardwood kraft pulp (UKP) was determined by the electron spin resonance (ESR) method. The spectrum of Mn(II), which revearled hyperfine splitting, was not observed, and the spectrum of dioxide could be observed. After fungal- treatment of UKP with *Phanerochaele sordida* YK-624, the spectrum of Mn(II) could be detected in the UKP. It is concluded that manganese dioxide is dominant in UKP, and that *P. sordida* YK-624 reduced manganese dioxide to Mn(II) which may stimulate production and function of manganese peroxidase.

1996-P16

イネワラのセルラーゼ及びアンモニアを用いたパルプ化とパルプの性状

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Preparation and characterization of rice straw pulps by cellulase or ammonia treatments

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Abstract: It is expected to develop the effective utilizations of agricultural wastes, such as rice straws, with environmentally sustainable processes. In this paper, pulping of rice straw by treatments with polysaccharide hydrolases or alkaligenic chemicals, but not by conventional alkaline treatments, were examined. The pulps were characterized by chemical analyses of the components, and their behaviors during laboratory scale defibration of treated rice straws were observed by SEM-EDXA. There were no significant improvements for defibration of rice straws by any enzyme treatments, but ammonia treatment which improved defibration and caused considerable deliglification probably due to the cleavage of ester-linkage between lignin and polysaccharides through ferulic acids, together with effective removal of silica from pulps. In addition we confirmed that all of *p*-hydroxybenzaldehydes in an alkaline nitrobenzene oxidation products of rice straw are produced from *p*-coumaric acids esterified or etherified to wall polymers, and lignin in rice straws is not characterized by the presence of *p*-hydroxyphenyl nuclei.

1996-P17

リグニン系土壌改良剤の開発（5）各種リグニンの添加と根の伸長生長

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Developmentof new lignin derivatives as soil conditioning agent (V), Growth of plants root under various soil condition containing lignin samples

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Abstract: It is well known that aluminium ion gives seriously damages to plant growth in acid soil. We have developed a new lignin derivative (radically sulfonated: S-1) from kraft lignin, which strongly associates with soil and also traps Al ion. So, there is a possibility of utilization of kraft lignin as a soil conditioning agent. In this paper, the length of roots of radish (*Raphanus Sativus*.) were determined during the growth on various soils containing lignin samples, and these effects on the growth of root were examined. As a results, all lignin samples apparently removed the inhibitory effects of aluminium ion. And, S-1 may be

more effective than LSA.

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1997-101

イネ培養細胞におけるヒドロキシケイ皮酸類の形成機構

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Formation of hydroxycinnamic acids in the suspension culture of *Oriza sativa*

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Abstract: Formation of hydroxycinnamic acids in the suspension culture of *Oriza sativa* was investigated. This culture was the cluster of a number of cells which did not have the secondary cell wall. It was shown ferulic acid was deposited in the cell wall at the early stage prior to the deposition of *p*-coumaric acid. Feeding experiment showed that labeled feru1ic acid was incorporated into cell wall as esterified ferulic acid selectively, while labeled *p*-coumaric acid was incorporated after the major conversion to ferulic acid. It was also suggested that considerable amount of ferulic acid fed to the culture was covalently linked at the 5 position of its aromatic ring during long term incubation.

1997-102

イネ節間柔組織形成異常 mutant を用いた細胞壁形成過程の解析

西窪伸之[*1]、荒木智之[*1]、藤川　裕[*1]、平田　豊[*2]、北野英己[*3]、黒田健一[*4]、片山義博[*1]
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Chemical and molecular biological analysis of cell wall formation in dwarf mutant of rice plant (Fukei-71)

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Abstract: Recessive mutations at single locus cause the collapse of parenchyma cells in internode of Rice plant “Fukei-7l”. This irregular parenchyma mutation was identified by gamma-ray irradiation of seed of "Fujiminori”. The mutated Rice plant "Fukei-71" show dwarf form and acuumulates lgnin- like material from *p*-coumaric acid and ferulic acid in parenchyma cell. The lignin-like material may be esterified cross-link between phenylpropanoids and polysaccharide. Furthermore existence of pathway related to ester cross-link separate from is suggested by strong expression of PAL and OMT of lignin biosynthesis pathway in parenchyma cell. This mutant is regarded as mutation participating in the factor that controls the cell wall formation with single regulation factor recessive at higher position than regulation of lignin and polysaccharide biosynthesis. The mutation should be useful in facilitating the identification of factors that control the synthesis and deposition of lignin and other cell wall components.

1997-103

イネ科植物リグニンにエーテル結合したヒドロキシ桂皮酸の結合位置

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Hydroxycinnamic acid bridges between wall polysaccharides and lignin in Gramineous plants

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Abstract: The hydroxycinmmic acids, *p*-coumaric (PCA) and ferulic acid (FA), are esterified and/or etherified to cell wall polymers in Gramineous plants, but of which position etherified to lignin side chain are not clear and argued for the α- or β-positions. In this study, lignin-polysaccharide complexes (bridges between lignin and wall polysaccharide through FA) extracted from walls of oat (*Avena sativa L.*) internodes were examined by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) oxidation followed by alkaline hydrolysis. The quantities of hydroxycinnamic acids liberated by alkaline hydrolysis were compared between before and after DDQ oxidation. Relatively high quantities of liberated FA and PCA after DDQ oxidation than those before DDQ oxidation suggests that they could etherify lignin at α-position of lignin side chain.

1997-104

Eucalyptus camaldulensis および *E. globulus* の樹幹内変異を用いたリグニン含有率、リグニンのモノマー組成比とヘミセルロース組成比の関係について

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Relationship of lignin content, and lignin monomeric composition and hemicellulose composition in the same trunk sought by their within-tree variations in *Eucalyptus camaldulensis* and *E. globules*

Toshihiro Ona, Tetsuya Sonoda, Kazuya Ito, Masaru Shibata
Kameyama Research Center, Forestry Research Institute, Oji Paper Co. Ltd.

Abstract: The relationship of extractives-free (EF) lignin content, lignin monomeric composition as syringyl/guaiacyl (S/G) ratio by thioacidolysis, and neutral sugars constituting hemicellulose by hydrolysis with trifluoroacetic acid was examined. This was performed in the same trunk by their within-tree variations, which mean the investigation with the same genes, in *Eucalyptus* camaldulensis and *E. globulus.* As results, each species had a high negative correlation between EF-lignin content and lignin S/G ratio although the difference between species and/or individuals was observed in the trend of within-tree variations of the wood properties. The relationship between EF-lignin content and lignin S/G ratio is considered to be caused from the difference in the fiber morphology from the relationship between lignin and EF-basic density which may relate to the fiber morphology. Furthermore, the relationship between the lignin monomeric composition derived from β-*O*-4 bonds and the hemicellulose composition is concluded to exist since common trend was observed between two species as higher lignin S/G ratio with the increase in xylan and or with decrease in arabinogalactan (galactan). We also discuss and suggest that the hemicellulose composition can influence on the lignin monomeric composition.

1997-105

Eucalyptus globulus Lignin の化学的性状　—改良ニトロベンゼン酸化—

片平　類、中坪文明
京都大学大学院農学研究科

The chemical characterization of *Eucalyptus globulus* lignin, — Analysis by a modified nitrobenzene oxidation —

Rui Katahira, Fumiaki Nakatubo
Graduate school of Agriculture, Kyoto University

Abstract: Recently, *Eucalyptus globulus* has been regarded as one of the most suitable trees for pulping, because it can grow largely in short time and gives a high yield of pulping. It is really important to find the reason for its high yield. Thus, we intended to investigate the chemical structure of *E.globulus* lignin. Here we propose a modified nitrobenzene oxidation method, which was applied to *E. globulus* lignin.

1997-106

超音波照射したリグニン溶液の ESR 法による研究　—スピントラッピング法の適用—

清野晃之、吉岡亜希、藤原政司、陳　克利、恵良田知樹、田畑昌祥、高井光男
北海道大学大学院工学研究科

An electron spin resonance study of radicals produced by ultrasonic irradiation of lignin solution. An application of spin-trapping method

Teruyuki Seino, Aki Yoshioka, Masashi Fujiwara, Ke-Li Chen, Tomoki Erata, Masayoshi Tabata, Mituo Takai
Graduate School of Engineen.ng, Hokkaido University

Abstract: A spin trapping technique combined with an electron spin resonance (ESR) method was successfully applied to the lignin solution which was subjected to ultrasonic irradiation in order to trap and identify the origin radical of the phenoxy radicals stabilized in the wood lignin. It was found, consequently, that nitroxide radicals called spin adducts produced by the reaction of secondary carbon radicals and 2,4,6-tri-*tert*-butylnitrosobenzenes as the spin trapping reagent were generated from the lignin dissolved in dimethysulphoxide (DMSO) when the lignin solution was subjected to ultrasonic irradiation at 50 ºC. The resulting secondary carbon radical was supposed to be created by the βbond scission in the HC^{β}-O-^{4}phenol group called β-*O*-4 bond which combines the three dimentional network structure of the wood lignin. Further the secondary carbon radical was also considered as a counter radical of the phenoxy radical stabilized in the not only solution but also lignin solid.

1997-107

リグニン化学構造の不均一性（2）—エーテル結合の選択的開裂を用いたリグニンの性状の検討—

堀啓映子、飯塚堯介
東京大学大学院農学生命科学研究科

Structural heterogeneity of hardwood lignin (II), —Characterization of lignin by selective cleavage of ether linkages—

Keko Hori, Gyosuke Meshitsuka
Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Trimethylsilyl iodide (TMSiI) was known to cleave α- and β- ether bonds selectively under mild condition. We used TMSiI to degrade high molecular weight lignin, and analyzed the newly formed low molecular weight fractions. It was found that there are some endwise lignin fractions in methylated-periodate lignin of birch, however it was not the case for birch MWL. Every low molecular weight fraction from MWL by TMSiI treatment showed quite similar characteristics. An end-wise lignin fraction from periodate lignin was confirmed to be depolymerized mainly to monomeric units by excess amount of TMSiI.

1997-108

CAD阻害によって形質転換させた樹木中に生成する異常リグニンの化学的構造について —種々の化学分解反応に対するシンナミルアルデヒド構造の挙動—

伊藤　隆[*1]、河合真吾[*1]、大橋英雄[*1]、樋口隆昌[*2]
[*1] 岐阜大学大学院連合農学研究科、[*2] 京都大学名誉教授

Chemical study on abnormal lignin of transgenic plants with antisense cinnamyI alcohol dehydrogenase gene, —The behavior of cinnamyl aldehyde groups for various chemical degradation reactions—

Takashi Ito[*1], Shingo Kawai[*1], Hideo Ohashi[*1], Takayoshi Higuchi[*2]
[*1] The United Graduate School of Agriculture Science, Gifu University, [*2] Professor emeritus Kyoto University

Abstract: Novel thioacidolysis products derived from sinapaldehyde and coniferyl aldehyde were isolated and identified by GC-MS and ^{1}H-NMR analyses, It is clear that the cinnamyl aldehydes were converted to many degradation products by thioacidolysis. On the other hand, sinapaldehyde and coniferyl aldehyde were not altered by acidolysis. The acidolysis treatment of coniferyl aldehyde DHP gave vanillin, coniferyl aldehyde and an unknown product as degradation lproducts. Coniferyl aldehyde and sinapaldehyde were effectively altered by mild alkali treatment to give vanillin and syringaldehyde, respectively.

1997-109

樹木細胞壁リグニン生合成及び糖代謝過程の免疫組織化学的研究

吉富圭織[*1]、増野洋子[*1]、西窪伸之[*1]、真壁和彦[*1]、川合伸也[*2]、諸星紀幸[*1]、片山義博[*1]
[*1] 東京農工大学大学院 BASE、[*2] 東京農工大学農学部

Immunohistochemistry of lignin biosynthesis and carbohydrate metabolism in woody plant

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[*1] Graduate School of Bio-Application and Systems Engineering, Tokyo University of Agriculture and Technology, [*2] Tokyo University of Agriculture and Technology

Abstract: Lignin is a major component of plant cell wall. We have investigated enzymes involved in the phenylpropanoid biosynthesis by biochemical and immunochemical methods. We prepared antiserums raise against PAL, OMT, 4CL, CAD, POX, and investigate immunochemical localization of these enzymes. As a result, we suggested the tissue-specific expression and relevance of each enzyme in protoxylem. We will report localization of each enzyme in metaxylem tissue and propose functions of them. Carbohydrate chain biosynthesis closely related to lignin biosynthesis in cell wall fomlation in plant. Therefor, we prepared antiserums raise against enzymes involved in the carbohydrate chain biosynthesis and investigate immunochemical relationship between lignin and carbohydrate chain biosynthesis.

1997-110

土壌微生物 *Sphingomonas paucimobilis* SYK-6 株のリグニン分解に関与するテトラヒドロ葉酸依存性脱メチル化酵素遺伝子（*lig H*）の構造と機能に関する研究

園木和典[*1]、笠原健秀[*2*3]、西川誠司[*4]、川合伸也[*2]、諸星紀幸[*1]、片山義博[*1]
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Structure and function of tetrahydroforic acid dependent *Sphingomonas paucimobilis* SYK-6 gene essential to degradation of lignin

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[*1]Graduate School of Bio-Application and Systems Engineering, Tokyo University of Agriculture and Technology, [*2]Tokyo University of Agriculture and Technology, [*3]Cosmo research institute, [*4]Nippon paper industries

Abstract: The soil bacterium, *Sphingomonas paucimobilis* SYK-6 is able to degrade various types of dimeric lignin compounds such as biphenyl, β-aryl ether, phenylcoumaran etc. In this study, we report here about the 1.8 kbp DNA fragment essential to *O*-demethylation of syringic acid (SA) and vanillic acid (VA). Sequencing analysis showed an open reading frame of 1671bp in this fragment, and this ORF has homolog to formyltetrahydrofolate synthetase. When this gene was expressed in mutant DC-49, which was deficient in demethylation of SA and VA, the enzymatic activity of VA and SA demethylation was observed. For enzymatic activity of *O*-demethylation of SA and VA, *lig H* and tetrahydroforic acid were essential.

1997-111

担子菌における菌体外ヘム酵素合成系の解析 —外因性 5-アミノレブリン酸の菌体外酵素分泌への影響-

松下啓太、割石博之、田中浩雄
九州大学農学部

Effect of exogenous 5-aminolevulinic acid on fungal production of extracellular heme peroxidases

Keita Matsushita, Hiroyuki Wariishi, Hiroo Tanaka

Abstract: Extracellular activity of heme peroxidases (LiP, MnP) was closely related to 5-aminolevulinic acid biosynthetic activity in white-rot fungi. ALA biosynthetic activity was higher in the white-rot fungi, *Coriolus versicolor* and *Phanerochaete chrysosporium*, than that in the brown-rot fungus, *Tyromyces palustris*. The effects of exogenous ALA on extracellular heme peroxidases were investigated. Exogenous addition of ALA increased the relative amounts of free protoheme and of secreted MnP. ALA had no effect on MnP activity. These results suggested that the rate- determining step for extracellular heme peroxidase production may not be protein but heme biosynthesis.

1997-112

ペルオキシラジカル及びスーパーオキサイドアニオンの関与する遷移金属錯体 —電子移動系反応によるリグニンの解重合—

渡辺隆司[*1]、Karin Koller[*2]、Kurt Messner[*2]、仲亀誠司[*1]、榎　牧子[*1]、本田与一[*1]、桑原正章[*1]
[*1] 京都大学木質科学研究所、[*2] ウィーン工科大学生物化学工学微生物研究所

Depolymerization of lignin by transition metal complex-electron transfer reactions involving peroxyl radical and superoxide anion

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[*1]Wood Rsearch Insdtute, Kyoto University, [*2]Research Institute for Biochemical Technology and Microbiology, University of Technology, Vienna

Abstract: In aqueous solutions, ^{14}C-labelled synthetic lignin was intensively depolymerized with
Cu(II) ad lipid hydroperoxide model compounds at room temperature in the presence of pyridine, which is known as a metabolite of lignin-degrading fungi. Reaction of Cu(II)/pyr with H2O2 was less effective for the lignin depolymerization, but this system enhanced the brightness of UKP frm 34.5 to 81 point. Spin trapping experiments demonstrated that peroxyl radical is involved in the former reaction while the latter involves superoxide anion and active oxidants other than hydroxyl radical. A wide variiety of practical application will be developed based on the copper/coordination compound/ peroxide reactions.

1997-113

リグニンペルオキシダーゼによるベラトリルアルコールの酸化機構

桃原郁夫
森林総合研究所

Veratryl alcohol oxidation catalyzed by lignin peroxidase

Ikuo Momohara
Forestry and Forest Products Research Institute

Abstract: Mechanism of veratryl alcohol oxidation catalyzed by lignin peroxidase was investigated.

Relationship between LiP inactivation and amount of veratraldehyde formation suggests that the amount of hydrogen peroxide consumed for inactivating LiP is negligible. Reactions under single turn over conditions suggest reaction of LiP-I with veratryl alcohol is necessary for veratraldehyde formation in the absence of oxygen. Stopped-flow technique reveals that two veratryl alcohol molecules are involved in Lip catalytic cycle.

1997-114
Lignin Peroxidase によるリグニンの直接酸化 −DHP と LiP compound I, II の反応性の検討—
城島 透、割石博之、田中浩雄
九州大学農学部
Direct oxidation of lignin by lignin peroxidase, – Reactivity of LiP compound I, II with DHP
Toru Johjima, Hiroyuki Wariishi, Hiroo Tanaka.
Faculty of Agriculture, Kyushu University

Abstract: Reactivity of lignin peroxidase (LiP) from *Phanerochaete chrysosporium* against a synthetic lignin (DHP) were studied utilizing transient kinetic technique. A one-electron transfer from DHP to LiP compound I (LiPI) exhibited saturation kinetics, from which the dissociation equilibrium constant for LiPI-DHP interaction was calculated to be 350 □M. Kinetic characterization of LiPI reaction with DHP strongly suggested that LiP is capable of oxidizing DHP directly at the protein surface via a long-range electron transfer process.

1997-特別講演
地球環境とバイオマス
戸倉清一
北海道大学大学院地球環境科学研究科
Sustainability of earth environment through biotechnology
Seiichi Tokura
Graduate School of Environmental Earth Science, Hokkaido University

Abstract: The higher quality of foods is requested due to rapid progress of human life, the more heavy environmental pollution is caused by a tremendous amount of food, agricultural and marine wastes. Several polysaccharides in these wastes have been studied as renewable resource due to relatively easier extraction and purification from waste. Chitin, one of biofunctional muco- polysaccharides of natural occurrence, has been investigated to apply for biomedical materials following to the removal of calcium and protein. Although waste paper is recycled in paper industry, cellulosic resources are able to find out easily in agricultural or food wastes. These cellulosic wastes were studied to reconstruct into novel polysaccharides with new functions through bacterial cultivation. The direct filamentation of novel polysaccharide has been achieved successfully by the use of shallow culture pan which was designed to form a thinner gel on the surface of culture medium. The filamentation was proceeded continuously with the rate of 30mm/h. The functionalization of cellulosic products were also achieved successfully with change of carbon source in the culture medium.

1997-201
トチュウの粗酵素によるネオリグナン・リグナンのエナンチオ選択的生成
加登優樹、片山健至
香川大学農学部
Enantioselective formation of neolignans/lignans by cell-free extracts of *Eucommia ulmoides*
Yuki Kado, Takeshi Katayama
Faculty of Agriculture, Kagawa University

Abstract: Formation of (+)-*erythro* and (-)-*threo* guaiacylglycerol-β-coniferyl ethers was found, following incubation of coniferyl alcohol with cell-free extracts from stems of *Eucommia ulmoides* young shoots in the presence of H2O2. Enantiomeric excesses of the both diastereomers increased in a Iinear fashion for l hr. When the (±)-*erythro* isomer was incubated as a substrate under the same conditions, it was recovered as an almost racemate. The *erythro* isomer formed by the action of cell-free extracts from the leaves was an almost racemate. Incubation of sinapyl alcohol with insoluble residues from the stems in the absence of provided cofactors gave syringaresinol with (+)-enantiomer slightly preferred.

1997-202
Linum flavum のリグナン生合成酵素について
三亀啓吾、梅澤俊明、島田幹夫

京都大学木質科学研究所

Lignan synthesis by cell-free extracts from *L.inum flavum*

Keigo Mikame, Toshiaki Umezawa, Mikio Shimada

Wood Research Institute, Kyoto University

Abstract: Three lignans, (+)-pinoresinol (65% e. e.), (+)-lariciresinol (70% e. e.) and (-)-secoisolariciresinol (>99% e. e.) were isolated from *Linum flavu*m. When [9,9-^{2}H2,OC^{2}H3] coniferyl alcohol was administered to this plant, incorporation of deuterium atoms into pinoresinol, lariciresinol and secoisolariciresinol was observed. Cell-free extracts from *Linum flavu*m catalyzed the formation of the three lignans, when incubated with coniferyl alcohol in the presence of NADPH and H2O2. These results suggested that the step to produce the optically pure lignan is the formation of secoisolariciresinol from lariciresinol in *L. flavu*m.

1997-208

ベンジル化木材樹脂の発泡性を支配する諸因子

平岡俊治、上田昌見、高見泰博、越島哲夫

日本化学機械製造株式会社

Foaming-regulating factors of benzylation reaction on wood.

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Japan Chemical Engineering & Machinery Co. Ltd.

Abstract: Foaming is one of the most interesting practical use of wood plastics. In the case of benzylated wood resins, it becomes the biggest advantages for use of the resin that the foaming can be performed without use of any plasticizers. The present investigations were conducted to make clear the principal production conditions of well-foamable benzylated resin: Foaming temperature depended on the softening or flow temperatures, and the most adequate at about 5ºC above the softening temperature. Ferric ion was found to catalyze the decomposition of benzylchloride and diminished extensively the foaming extent of the benzylated wood resins. The influences of mercerization temperature were one of the biggest factors, and the extensive foaming appeared at 20 to 46ºC. Above 50ºC, foaming decreased less than 40% owing to liberation of lignin moiety from the LCC contained.

1997-204

リグニン含有型吸水性ポリウレタンフォームの形態的及び物理的性質

畠山兵衛[*1]、伊豆田良信[*1]、兼松幹生[*1]、廣瀬重雄[*2]、畠山立子[*2]

[*1] 福井工業大学工学部、[*2] 物質工学工業技術研究所

Morphological and physical properties of water-sorption type polyurethane foams containing lignin

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[*1]Fukui Institute of Technology, [*2]National Institute of Materials and Chemical Research

Abstract: Polyurethane (PU) foams were prepared from molasses (MOL), kraft lignin (KL) and an organosolv lignin (Alcel lignin, AL). The prepared PU foams were analyzed by differential scanning calorimetry (DSC), thermogravimetry (TG) and mechanical measurements. Using the obtained results, water-sorption type PU foams were prepared. The prepared PU foams showed thermal degradation temperature (*Td*) at around 220 - 230 ºC. Water absorptivity (W_s) was calculated according to the following equation: $W_s=(W_1- W_o)/V$, where W_o is weight of dry sample (g), W_1 weight of sample after water-absorption (g), V volume of dry sample (cm^3). W_s of the prepared PU foams depended on the density of sample and a maximum value was ca. 0.9. Stress/density value (kPa/kg±·m^{-3}) of dry sample was ca. 1.9 and ca 1.7 after water-absorption.

1997-205

リグニンベースポリカプロラクトン誘導体からのポリウレタンの調製と熱的性質

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[*1] 福井工業大学工学部、[*2] 物質工学工業技術研究所

Preparation and thermal properties of polyurethanes derived from lignin-based PCL

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[*1]Fukui Institute of Technology, [*2]National Institute of Materials and Chemical Research

Abstract: Polyurethane (PU) sheets were prepared from kaft (KL) and Alce1 (AL) lignin-based polycarprolactones (PCL). The obtained lignin-based PCL's were analyzed by differential scanning calorimetry (DSC) and thermogravimetry (TG). The glass transition temperature (Tg) decreased from -10 to -60 ºC with increasing CL/OH ratio from 2 to 25 mol/mol. The cold-crystallization and melting were observed when CL/OH ratio of the samples exceeds 15 mol/mol. DSC results suggest that CL molecules form crystalline structure by molecular rearrangement occurred at around 0 ºC. Phase diagrams were established for both KL and AL lignin-based PCL's.

1997-206

タンニン—タンパク質沈澱機構

河本晴雄[*1]、中坪文明[*2]
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Tannin-protein co-precipitation mechanism

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Abstract: Stoichiometric analysis of successive washing of galloylglucose (hydrolysable tannin) - protein precipitates by aqueous solution was carried out. The following results were obtained: 1) at least two bindings, strong and weak bindings, respectively, are included in the galloylglucose-protein bonds; 2) although maximum number of the binding site on a protein molecule increases linearly with an increase in protein molecular weight, content of the number of the strong binding sites (NSB) is quite different depending on the protein structure; this explains different relative affinities of proteins for tannin; 3) stability of the precipitates is explainable by the relationships between galloylglucose/protein molar ratio required for the precipitation and NSB.

1997-207

高分子量 procyanidin gallate の合成とその性質

米田　聡、中坪文明
京都大学大学院農学研究科

Synthesis of procyanidin gallates with high molecular weight and their function

Satoshi Yoneda, Fumiaki Nakatsubo
Graduate School of Agriculture, Kyoto University

Abstract: The preparation methods of the high-molecular-weight procyanidin gallate was developed. These methods may be also applicable to the conversion of lignins into the functional polymer with protein-precipitating capacity like tannins.

1997-208

炭素化非木材繊維シートの物性

大谷慶人、中島綾子、鮫島一彦
高知大学農学部

Characterization of resin-impregnated and carbonized nonwood fiber sheets

Yoshito Ohtani, Ayako Nakajima, Kazuhiko Sameshima
Faculty of Agriculture, Kochi University

Abstract: Ten nonwood bleached chemical pulps and one softwood bleached kraft pulp were used to make handsheets. All pulps were beaten by PFI mill and also subjected to handsheet making. Every handsheet was impregnated with phenol resin, polymerized by heating and carbonized at 800ºC. Resulting carbonized pulp sheets were characterized and evaluated as an electromagnetic shielding material. The sheets from bagasse, kenaf and jute pocessed good electric wave shielding effects rather than the cupper sheet. But the magnetic shielding effects were inferior to that of cupper sheet. The electric wave shielding effect correlates to the sheet thickness and density.

1997-209

Ganoderma sp. YK-505 株の産生するマンガンペルオキシダーゼの安定性について

原園幸一、近藤隆一郎、坂井克己
九州大学農学部

Stability of manganese peroxidase secreted from *Ganoderma* sp. YK-505

Koichi Harazono, Ryuichiro Kondo, Kokki Sakai
Faculty of Agriculture, Kyushu University

Abstract: We evaluated stabilities of manganese peroxidases (MnPs) secreted from white rot fungi, *Phanerochaete chrysosporium*, *Phanerochaet sordida* YK-624 and *Ganoderma* sp. YK-505. Two MnP

isoenzymes (G-1 and G-2) from *Ganoderma* sp. YK-505 exhibited stabilities against high temperature and pH. Change in the heme environment of MnPs from *Ganoderma* sp. YK-505 during incubation at high temperature and pH was investigated by electronic absorption spectroscopy. The absorption spectra of MnPs after incubation at high temperature or pH were similar to those of low-spin hexacoordinate ferric heme proteins, as described previously in the report that MnP from *P. chrysosporium* was very susceptible to thermal inactivation due to the loss of calcium from the enzyme. The results demonstrated that the same structural changes as MnP from *P. chrysosporium* occur during inactivation, resulting from the release of calcium from MnPs from *Ganoderma* sp. YK-505 although inactivation of MnPs from *Ganoderma* sp. YK-505 occur in severer condition than that of MnP from *P. chrysosporium*,

1997-210

担子菌 *Bjerkandera adusta*（ヤケイロタケ）の生産するマンガンペルオキシダーゼの有機溶媒中における反応

茶谷明伸[*1]、吉田晋一[*2]、本田与一[*1]、渡辺隆司[*1]、桑原正章[*1]
[*1] 京都大学木質科学研究所、[*2] 鳥取県工業試験所

Reaction of manganese-dependent peroxidase from *Bjerkandera adusta* in organic solvents

Akinobu Chatani[*1], Shinichi Yoshida[*2], Yoichi Honda[*1], Takashi Watanabe[*1], Masaaki Kuwahara[*1]
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Abstract: To characterize activities of manganese-dependent peroxidase (MnP) in organic media, aromatic compounds and DHPs were oxidized with MnP from *Bjerkandera adusta* in water-miscible organic solvents. ln 70% aqueous organic solvents, MnP exhibited high activities toward several phenolics and aromatic amines such as guaiacol, 2,6-dimethoxyphenol, 3,3.-dimethoxybendizine, *o*-phenylenediamine and *m*-aminophenol. Oxidation of DHPs by MnP was also observed in aqueous organic solvents. ln 70% acetone, guaiacyl DHP was polymerized by MnP while syrigyl DHP was depolymerized with concomitant formation of a small amount of polymerized compounds.

1997-211

白色腐朽菌のリグニン分解に関与する酵素系に関する研究（XIII）—白色腐朽菌の産生する siderophore 様物質について—

平井浩文、近藤隆一郎、坂井克己
九州大学農学部

Studies on ligninolytic enzymes of white-rot fungi (XIII), - Siderophore-like compounds produced by white-rot fungi

Hirofumi Hirai, Ryuichiro Kondo, Kokki Sakai
Faculty of Agriculture, Kyushu University

Abstract: We primarily tried to detect and isolate siderophore-like compounds from white-rot fungus *Phanerochaet sordida* YK-624. Fe(II) binding ability ms detected in 70% acetone-insoluble fraction from the liquid culture without Fe. The siderophore-like compounds were also secreted under Fe-sufficient culture. Two compounds (compound I and II) were purified from the fraction with gel permeation chromatographies. The molecular weight of these compounds were estimated about 3000-5000. IR spectra of these compounds showed the presence of both peptide bonds and alcoholic hydroxyl groups. It is suggested that these compounds selectively bound iron or cobalt. The addition of these compounds to the reaction mixture of ferrireductases accelerated consumption of NADPH.

1997-212

白色腐朽菌 *Phanerochate sordida* YK-624 株より得られた突然変異体によるクラフトパルプのバイオブリーチング

石村大児、近藤隆一郎、坂井克己、平井浩文
九州大学農学部

Biobleaching of kraft pulp with mutants from white-rot fungus *Phanerochaete sordida* YK-624

Daiji Ishimura, Hirofumi Hirai, Ryuichiro Kondo, Kokki Sakai
Faculty of Agriculture. Kyushu University

Abstract: We isolated mutant 1 and mutant 2 which have weak and strong tetrazolium salts reductive activity, respectively from *Phanerochaete sordida* YK-624 by UV irradiation. When unbleached hardwood and oxygen-bleached softwood kraft pulps were treated with wild type and these mutants, mutant l made highly pulp brightness increasing and secreted more manganese peroxidase (MnP) in the early incubation period compared

with wild type, although mutant 2 showed the same tendency as wild type. Mutant 1 secreted MnP under lower Mn(II) concentration, and uptook Mn(II) faster than wild type.

1997-213
The study on the ^{13}C-NMR spectra of dissolved lignin from Na$_2$S pretreatment kraft cooking
金　永燦[*1]、李　忠正[*1], Diesheng Tai[*1]、佐渡　篤[*2]
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The study on the ^{13}C-NMR spectra of dissolved lignin from Na$_2$S pretreatment kraft cooking. Yongcan Jin[*1], Zhongzheng Lee[*1], Diesheng Tai[*1], Atsushi Sawatari[*2]
[*1]Nanjing Forestry University, [*2]Faculty of Agriculture, Tokyo University of Agriculture and Technology

Abstract: Kraftban lignins from Na2S pretreatment liquor and cooking black liquor were isolated and analyzed by ^{13}C-NMR spectroscopy. The results were compared with those from conventional kraft cooking with similar degree of delignification. Kraft lignin from Na2S pretreatment liquor contains less etherified structures than that from conventional cooking. This indicates that the lignin removal during the Na2S pretreatment is different from that in normal kraft cooking. The structure of lignin from pretreatment liquor differs appreciably from that of lignin obtained from conventional pulping. Because of the relatively mild condition, a large amount of terminal groups in the lignin molecule are removed one by one as peeling reaction in the Na2S pretreatment. In contrast, the fragmentation of lignin is more random in the conventional kraft cooking.

1997-214
リグニンのオゾン酸化に伴う過酸化水素の生成
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Generation of hydrogen peroxide during the ozonation of lignin
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Abstract: Ozone reacts with lignin through two pathways. One is ionic cyclo-addition to cleave a C3-C4 double bond. This reaction generates hydrogen peroxide as a reaction product. Another way is one-efectron transfer from a dissociated phenolic hydroxyl group. This reaction reads to the formation of hydroxyl radicals which cause the non-selectivity of ozone reaction. In the case of the radical reaction pathway, hydrogen peroxide will not be produced. To investigate the contribution of these two pathways, we determined the generated hydrogen peroxide. When 2 mmol of veratryl alcohol was reacted with excess amount of ozone, 4.7mmol of hydrogen peroxide was detected. On the other hand, vanillyl alcohol gave only 0.7mmol of hydrogen peroxide under the same reaction conditions. In the case of veratryl alcohol, because of the lack of phenolic hydroxyl group, the ionic reaction pathway dominated. Although the dissociation of phenolic hydroxyl groups is very little under neutral conditions, the radical reaction pathway dominated in the case of ozonation of vanillyl alcohol. This is probably because the radical reaction is much faster than the ionic reaction.

1997-215
酸素脱リグニンに影響を与える要因 –溶解性有機物とリグニン量のばらつき-
種田英孝, 飯嶋純フェルナンド
日本製紙株式会社
Effect of several factors on oxygen delignification,–Carryover and lignin contents variation in fibers Hidetaka Taneda, Jun Fernando Iijima
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Abstract: The process factors which affect the delignification in a medium consistency oxygen delignification process were investigated. The effect of carryover to oxygen process consisted of the negative one by the organic compounds like lignin and the positive one by residual alkali in it. After the initial reaction with oxygen, COD and TOC values of the effluent did not change greatly. Therefore the further oxidation with oxygen did not observed. The variation of the lignin contents in each fiber showed the positive effect on the delignification in the case of oxygen delignification. The reason for this phenomena is under investigation.

1997-216
酸素系の漂白過程における活性酸素種の反応経路と反応選択性

横山朝哉、松本雄二、飯塚堯介
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Reaction route and reaction selectivity of active oxygen species in oxygen containing bleaching processes
Tomova Yokoyama, Yuji Matsumoto, Gvosuke Meshitsuka
Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: A cellulose model compound, methyl β-D-glucopyranoside (MGP), and/or lignin model compounds were subjected to a reaction in an alkaline hydrogen peroxide solution. The initial concentration of MGP and the presence of a lignin model compound did not affect the recoveries of MGP. Recoveries of MGP were smaller when hydrogen peroxide was stepwisely added than when hydrogen peroxide was added at once initially. These results confirmed a competition between model compounds and hydrogen peroxide in reacting with active oxygen species which were produced from the degradation of hydrogen peroxide itself, and suggested that active oxygen species attacked hydrogen peroxide preferentially rather than model compounds. The competition was observed most clearly when ferric ion was added.

1997-217
フエノキシラジカルと酸素との反応性について（2）
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Reactivity of phenoxyl radical with molecular oxygen, (2)
Tomoko Sugimoto, Yuji Matsumoto, Gyosuke Meshitsuka
Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: In order to examine the possibility of the reaction between phenoxyl radical and molecular oxygen, syringyl alcohol (SA) was treated with a one electron oxidizing reagent, manganese (III), and the effect of oxygen pressure on the yield of methanol from this phenol was determined. The increased formation of methanol under increased oxygen pressure was thought to indicate the reaction between phenoxyl radical and molecular oxygen. The yields of the starting material SA and one of the reaction products, syringaldehyde, were constant regardless of the oxygen pressure. Post-treatment with alkali was essential for the complete formation of methanol. The reduction by NaBH4 after the sufficient alkali-treatment resulted in increased formation of methanol. This is due to the reduction of formaldehvde formed by the coupling reactions of C1 radical.

1997-218
塩素漂白で生成した高分子有機塩素化合物の環境中での挙動（1）—熱分解ガスクロマトグラフによる分析法の確立—
幸田圭一、新谷博幸、松本雄二、飯塚堯介
東京大学大学院農学生命科学研究科
Environental fate of high molecular weight chloroorganics produced by chlorine bleaching (1) : Development of a new analytical method by the use of pyrolysis gas chromatography
Keiichi Koda, Hiroyuki Shintani, Yuji Matsumoto, Gyosuke Meshitsuka
Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: High molecular weight chloroorganics were extracted from chlorinated pulps by the use of aqueous dioxane and were used as authentic samples of chloroorganics in the effluent. The extracted chloroorganics were subjected to pyrolysis GC. The pyrogram of chloroorganics is quite different from that of milled wood lignin (MWL), which is assumed to be representative of the native lignin in wood. Over five hundred of pyrolysis products were detected in the GC and their mass fragmentation patterns were stored in the mass library. Interestingly, the majority of the pyrolysis products were not aromatics. By the use of the mass library thus constructed, samples obtained from the discharged bleaching effluents were successfully analyzed.

1997-219
塩素漂白過程で環開裂した芳香核に由来する低分子化合物の検出
新谷博幸、松本雄二、飯塚堯介
東京大学大学院農学生命科学研究科
Liberation of low molecular weight compounds from oxidatively cleaved aromatic ring of chlorolignin
Hiroyuki Shintani, Yuji Matsumoto, Gyosuke Meshitsuka
Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Unbleached softwood kraft pulp, unbleached hardwood kraft pulp and oxygen prebleached hardwood kraft pulp were chlorinated, and residual chlorolignin in pulps were extracted by aqueous dioxane. When extracted chlorolignins were treated with alkali, formic acid, glycolic acid, acetic acid and carbon dioxide were produced. These low molecular weight compounds should be liberated from the muconic acid type structure or its delivertives which were produced by the oxidative cleavage of aromatic ring during chlorine bleaching.

1997-P01
脱成分処理によるコルク細胞壁微細構造の変化
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Ultrastructure and histochemistry of phellem cell wall after solvent extraction and depolymerizations
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Faculty of Agriculture, Kyoto University

Abstract: Phellem, or cork tissue, of tree bark is well known to have suberized cell walls. It is accepted that suberin layers have polymeric suberin and soluble waxes, and that they appear as a fine lamellar structure in transmission electron microscopy. In this study, to clarify the relationship between chemical components and fine lamellar structure, removing process of cell wall components were observed in detail. Wax extracting with chloroform-methanol mixture at room temperature did not affect the lamellar structure, Whereas electron translucent lamellae are not observed after the extraction at 60ºC. KOH saponification for a brief time disrupted partially the lamellar structure. Possible explanadons for these observations are discussed.

1997-P02
ニトロベンゼン酸化後のヒノキ材細胞壁の構造
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Structure of cell walls after nitrobenzene oxidation in *Camaecyparis obtusa* Endl
Seizo Ohno, Arata Yoshinaga, Minoru Fujita
Graduate School of Agriculture, Kyoto University

Abstract: In alkaline nitrobenzene oxidation, degree of condensation in lignin has been evaluated from total yields of the oxidation products. The condensed units in lignin is expected to be resistant to the nitrobenzene oxidation. To clarify delignification process, wood sections after nitrobenzene oxidation with various reaction time were observed under an UV microscope, a SEM, and a TEM. As a result, the major part of lignin was removed from cell walls by the oxidation. This result suggested that condensed lignins were removed from cell walls by the cleavage of non-condensed units.

1997-P03
ニトロベンゼン酸化後の数種の広葉樹材細胞壁の構造
吉永　新、藤田　稔
京都大学大学院農学研究科
Structure of cell walls after nitrobenzene oxidation in several hardwoods
Arata Yoshinaga, Minoru Fujita
Graduate School of Agriculture, Kyoto University

Abstract: Alkaline nitrobenzene oxidation has been used as a useful means of characterizing monomeric composition and also degree of condensation of lignin. However, syringaldehyde / vanillin molar ratio (S/V ratio) obtained from the nitrobenzene oxidation provides information on only a part of lignin. To clarify behavior of the whole lignin during nitrobenzene oxidation, lignin distribution in cell walls were examined on several hardwoods after the nitrobenzene oxidation using UV microscopy and transmission electron microscopy. As a result, in both vessel elements and wood fibers, the major part of lignin was removed from cell walls by the oxidation.

1997-P04
ラジオトレーサー法によるリグニン試料調製中のペクチンおよびキシランの挙動の解明
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Behaviors of pectin and xylan during lignin preparations studied by radiotracer technique
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Abstract: Pectin and xylan were labeled with ^{14}C and 3H respectively by administration of D-glucuronic acid-[6-^{14}C] and *myo*-inositol-[2-^{3}H] to a growing stem of magnolia. The doubly radio-labeled wood meal was subjected to preparations of Klason lignin and milled wood lignin (MWL), and the radioactivities of the various fractions were determined to compare the behaviors of pectin and xylan during the preparations. Value of ^{3}H/^{14}C of the Klason lignin was smaller than that of original wood meat, and the value of the soluble part was larger that of the original. While, the ^{3}H/^{14}C value of the MWL fraction was smaller than that of the original, and the value of the lignin-carbohydrate-complex (LCC) fraction was near to the original value. These results indicate that pectin and xylan behaved differently during the lignin preparations, and pectin were ready to remain in Klason lignin and MWL compared with xylan.

1997-P05

リグニン前駆体とペルオキシダーゼの親和性と反応性

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Affinities and reactivities between monolignols and peroxidase
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Abstract: To clarify biosynthetic process of lignin, we studied affinities and reactivities between monolignols (*p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol and horseradish peroxidase (HRP). Affinities and reactivities were defined as k_{+1}/k_{-1} and k_{+2} of enzyme reaction, respectively. Affinities and reactivities between monolignols and HRP were reduced by increases number of methoxyl groups. However, the reduction of reactivity was extremely larger compared with the reduction of affinity.

1997-P06

フェノール性 β-O-4 型ジリグノール合成法の改良

置田恭子、飛鳥井雅倫、田中　愛、杉下千洋、河合真吾、大橋英雄
岐阜大学農学部

The convenient synthetic method of β-O-4 dilignols
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Faculty of Agriculture, Gifu University

Abstract: Lignin substructure model compounds, especially β-O-4 dilignols, play important role for biodegradation and structural studies of lignin. Many synthetic routes were reported, but these methods need chloric solvents which have been forbidden for environment problems, different protecting groups for the reactivity between guaiacyl and syringyl nuclei and/or strict anhydrous condition. To make up for such disadvantages, we tried a few modification based on method of Adler and Eriksson. This convenient method has relatively short reaction time and high yields without strict anhydrous conditions, chloric solvents and drastic reagents.

1997-P07

近赤外フーリエ変換ラマン分光法によるリグニン中の α および γ 位のカルボニル基の定性および定量

高山　幸、割石博之、田中浩雄
九州大学農学部

FT Raman spectroscopic characterization of carbonyl groups in lignin
Miyuki Takayama, Hiroyuki Wariishi, Hiroo Tanaka
Faculty of Agriculture, Kyushu University

Abstract: A near infrared fourier transform Raman (NIR-FTR) spectroscopic technique was utilized to characterize lignin. The ν(C=O) band, which could be a good monitoring probe to follow wood deterioration, can be seen as an isolated sharp band with medium intensity on NIR-FTR spectra of wood. On the other hand, it has been known to give a broad absorption with strong intensity on FTIR spectra. DHP prepared from coniferaldehyde exhibited a band at 1620 cm^{-1}, while DHP prepared from coniferyl alcohol did not show this band. In NIR-FTR spectra of MWL and wood meals 1620cm^{-1} disappeared as reduction with NaBH4. From these results, this band was assigned to γ-carbonyl band.

1997-P08

Cloning of novel cytochrome P450 monooxygenase in quaking aspen (*Populus tremuloides*)

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Abstract: Using a modified mRNA differential display technique to analyze differentially expressed P450 genes in the 6th to 10th internodes that were absent in the 1st to 4th internodes of young aspen shoots, we cloned a full-length cDNA (asc6), which encodes a typical P450 of 508 amino acids. The deduced asc6 protein sequence shows a less than 40% sequence identity with all other known plant P450s in DNA databases. Thus, asc6 can be considered to represent a novel class of P450.

1997-P09

カワラタケ（*Coriolus versicolor*）菌体外粗酵素によるカテキン類の変換とその Gtase 阻害活性

西田容子、光永　徹、船岡正光
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Conversion of catechins by the extracellular enzymes of *Coriolus versicolor* and inhibitory action of converted compounds on GTase

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Faculty of Bioresources, Mie University,

Abstract: The chemical structures of bioconverted compounds from catechins by *Coriolus versicolor* and their inhibitory activities on glucosyltransferase (GTase), relating to the generation of dental caries are examined. Dimeric compounds Y-2, Y-3 from (+)-catechin and trimer Y-4, dimer Y-5 from (-)-epicatechin were produced. According to the NMR data, oxidative coupling occurred between A ring and B ring of catechins to generate a conjugated carbonyl group in the molecules. In spite of the dimeric classes the converted compounds showed high inhibitory activities on GTase, especially Y-3 and Y-5 were remarkable. The MM2 energy calculation of these compounds showed a good correlation between stretch-bend energy and GTase inhibitory activity. Therefore, it was presumed that the planar and strained structure is one of the important factor on GTase inhibitory action.

1997-P10

CAD 遺伝子を導入したタバコでの CAD の分布

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Localization of CAD in CAD gene induced tobacco cell

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Abstract: Considerable works has revealed the presence of enzymes involved in lignin biosynthesis, and the biosynthetic pathway of lignin is, now, generally accepted. However, the localization of each enzyme in the cell, the regulation of the synthesis of each enzyme and the transporting mechanism of lignin precursors are unresolved. Cinnamyl alcohol dehydrogenase (CAD) is the final enzyme for the synthesis of monolignols. This enzyme catalyzes the reduction of cinnamaldehydes to their corresponding cinnamyl alcohols. Immunocytochemistry revealed the difference of CAD distribution between the normal tobacco cell and the CAD gene induced tobacco cell. The latter showed the remarkable increase of labelling in cyto-sol. The labelling was also observed on the cell wall in both cells. From above results, localization and role of CAD were discussed.

1997-P11

植物培養細胞を用いたバイオトランスフオーメーションによる有用物質の生産

坪田弘志、伊藤和貴、橘　燦郎
愛媛大学農学部

Production of useful substances by biotransformation with plant cell cultures

Hiroshi Tsubota, Kazutaka ltoh, Sanro Tachibana
Faculty of Agriculture, Ehime University

Abstract: Production of pinoresinol diglucoside from pinoresinol by cell suspension cultures of *Coffea*

arabica was tried. From the results of HPLC analyses of the reaction products, we found that pinoresinol diglucoside was produced from pinoresinol in the maximum yield of 33.6% by the cultures
of *C. arabica*. We also found that the concentrations of the substrate added to the cultures was lower, the yields of the glucoside was higher. However, the yields of the glucoside was higher. However, the yields of the yields of the glucoside decreased with the incubation time.

1997-P12

数種の植物懸濁培養細胞を用いたフェノール性化合物のバイオトランスフオーメーション

好川　恵、光度知代、伊藤和貴、橘　燦郎
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Biotransformation of phenol compounds by some plant cell suspension cultures
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Faculty of Agriculture, Ehime University

Abstract: Production of phenol glucosides from two phenols, 4-methoxy phenol and scopoletin by cell suspension cultures of *Coffea arabica*, *Nicotiana tabacum* and *Vinca rosea* were tried. From the results of HPLC analysis of each reaction product, we found that methylarbutin, phenolic glucoside of 4-methoxy phenol was produced from 4-methoxy phenol in the maximum yield of 22.7 % and 15.6 % by the cell suspension cultures of *C. arabica* and *N. tabacum*, respectively. Scopolin, glucoside of scopoletin could be produced from scopoletin by the cell suspension cultures of *V. rosea*, however, the maximum yield of scopolin was 2.6 % of the added substrate.

1997-P13

原子間力顕微鏡を用いたクラフトパルプ表面の観察　—脱リグニンが表面性状に及ぼす影響—

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Observation of the surface of kraft pulp fibers by atomic force microscopy, — Influence of deligniflcation on the character of the surface of kraft pulp fibers
Tetsuaki Okamoto, Gyosuke Meshitsuka
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Abstract: The surfaces of unbleached kraft pulp and some treated kraft pulp fibers were observed by contact mode AFM in the air. Clear and high-resolution images of AFM of fine fibrils were obtained. The size of fine fibrils was estimated to be 2-5nm according to the artifact by tip-sample convolution. Apparent swelling of fine fibrils was observed in the case of Cl2-alkali treated sample probably due to the removal of lignin and hemicellulose during the treatment.

1997-P14

酸素漂白過程における共酸化現象の評価

童　国林、横山朝哉、松本雄二、飯塚堯介
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Oxygen oxidation of non-phenolic lignin units by a co-oxidation mechanism
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Abstract: Kraft lignin and isolated residual lignin from unbleached softwood kraft pulp were subjected to oxygen-alkali oxidation, and the extent of the oxidation were evaluated by permanganate consumption of oxidized lignin. The residual lignin was much more easily oxidized by oxygen-alkali than kraft lignin. Three phases are observed during the oxidation of the isolated residual lignin. The first phase was the fastest and most of electrons (about 5) were lost in this phase. The lost electrons during total three phases were 9 per lignin unit. Model experiments by the use of phenolic and non-phenolic lignin model compounds confirmed that even a non-phenolic unit can be oxidized during oxygen-alkali treatment by the co-oxidation mechanism. However, the extent of oxidation of the model system which contains equimolar amount of phenolic model and non-phenolic model compound was much smaller than the extent of oxidation of the isolated residual lignin.

1997-P15

生ゴミ処理スギチップのリグニン、ノルリグナンの変化とパルプ化に及ぼす影響

島田謹爾[*1]、加藤　厚[*1]、富村洋一[*1]、真柄謙吾[*1]、大原誠資[*1]、石原光朗[*1]、福田清春[*2]

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Changes of lignin and norlignans of Sugi (*Cryptomeria japonica*) chips during the garbage treatment and their effects on kraft pulping

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Abstract: To investigate the changes of lignin and norlignans of Sugi (*Cryptomeria japonica*) chips during the treatment of garbage, the alkaline-nitrobenzene oxidation products were analyzed by means of GLC,^{1}H and ^{13}C-NMR spectroscopy. In addition, the effects of the changes of them on kraft pulping was also examined. Following results were obtained. 1) The yield of total aldehydes on nitrobenzene oxidation decreased in the treated chips. 2) The yields of the oxidation products of treated chip were higher for *p*-hydroxybenzaldehyde and lower for methoxyl group than those of non-treated chip. This result implies that the polymerized norlignans have remained in the chip and decomposed on nitrobenzene oxidation to yield *p*-hydroxybenzaldehyde. 3) In the initial stage of kraft pulping, the treated chip was well cooked and the delignification proceeded faster than the non-treated chip. In the last stage, however, the large amounts of lignin remained in the pulp. 4) Both the changed lignin and norlignans could not be easily removed during the pulping process.

1997-P16

担子菌による含硫黄ヘテロ環化合物の変換 —基質認識および代謝応答—

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Biotransformation of sulfur containing heterocyclic compounds by basidiomycetes, - Substrate recognition and metabolic response

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Abstract: Lignin degrading basidiomycete *Coriolus versicolor* was utilized to degrade sulfur containing heterocyclic compounds which are recalcitrant compounds found in fossil resources. The transformation of these compounds by *C, versicolor* were occurred in different manner under different metabolic conditions. Nonaromatic compounds such as 2-hydroxymethylthiophene were metabolized in primary metabolic conditions and utilized as a sulfur source for growth. While aromatic compounds such as 2-hydroxymethylbenzothiophene and 4-methyldibenzothiophene were metabolized as xenobiotic detoxification. It was suggested that substrate recognition controls the metabolic response.

1997-P17

担子菌原形質膜機能解析モデルへのプロトプラストの適用

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Utilization of fungal protoplasts as a plasma membrane model for functional analysis

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Abstract; White-rot basidiomycetes are capable of degrading lignin. The extracllular lignin degrading enzymes catalyze the depolymerization of lignin. But a little is known about mechanism of uptake of lignin degradation fragments. As an active plasma membrane model, we attempted to utilize protoplasts. In this study, we analyze the reduction of quinones and uptake of lignin degradation fragment using protoplasts prepared from a brown-rot basidiomycete. 2,6-Dimethoxy- 1,4-benzoquinone and 2,5-dihydroxy-1,4-benzoquinone were effectively reduced by protoplasts and formed 1,4-dihydroxy-2,6-dimethoxybenzene and 1,2,4,5,-tetrahydroxybenzene, respectively. Syringaldehyde, syringic acid and protocatechuic acid was not converted into other compounds. However, only protocatechuic acid was detected intracllularly, showing the selective permeability of fungal plasma membrane.

1997-P18

絶対嫌気性ルーメン細菌による非フェノール性ベンジルエーテルの解裂

渡辺隆司[*1]、梶川　博[*2]、工藤　博[*2]、近藤恒夫[*3]、城代　進[*4]、中島由美[*1]、本田与一[*1]、桑原正章[*1]

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Cleavage of non-phenolic benzyl ether bonds by strictly anaerobic rumen bacteria

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Abstract: Fluorescent benzyl ether model compunds with non-phenolic unit were chemically synthesized. The models were incubated with rumen microorganisms under anaerobic conditions in the presence and absence of bactericidal and fungicidal antibiotics. Fluorescent spectrometry of the culture fluid showed that the non-phenolic benzyl ethers were rapidly cleaved by strictly anaerobic rumen bacterial fraction.

1997-P19

白色腐朽菌によるポリエチレンの分解（III）

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Polyethylene degradation by white rot fungi

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Abstract; We previously reported that polyethylene degradation by manganese peroxidase (MnP) required Tween 80 or 20 and Mn(III) generated from Mn(II) in the MnP catalytic cycle but not H2O2 which is recognised to be indispensable for the generation of Mn(III) by MnP. In this study, therefore, Mn(III) formation by MnP without exogenous H2O2-supply was investigated. Neither Tween 80 nor Tween 20 affected on the Mn(III) formation by MnP very much. The Mn(III) formation was slightly accelerated under oxygen atmosphere, but was strongly restrained under nitrogen atmosphere. Addition of catalase into MnP reaction mixture to decompose endogenous H2O2 did not inhibit the Mn(III) formation. These results indicate that Mn(III) formation by MnP in polyethylene degradation is dependent on oxygen under the condition without exogenous H2O2.

1997-P20

Differential Display 法による、カワラタケの有害化学物質分解関連遺伝子の検索

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Isolation of mRNAs induced by a hazardous chemical in white-rot fungus, *Coriolus versicolor*, by differential display

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Abstract; White-rot fungus *Coriolus versicolor*, a ligninolytic basidiomycete, has been studied because of its ability to degrade hazardous chemicals. In this study, we searched for genes that are induced by a hazardous chemical using the mRNA differential-display technique arid C. *versicolor* IFO30340 that has been exposed to pentachlorophenol (PCP). Five cDNA frgments were cloned and the DNA sequences of two fragments were analyzed in further detail. The clones corresponded to novel genes that have not previously been identified in *C. versicolor*. One of the cDNAs exhibited homology to a heat shock protein. The expression of the gene was up-regulated in PCP-treated *C.versicolor*.

1997-P21

リグニン系土壌改良剤の開発（6）—改質リグニンの金属イオンとの相互作用—

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東京大学大学院農学生命科学研究科

Development of lignin derivatives as soil conditioning agents (6), - Interaction between modified lignins and metal ions

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Abstract; Soil conditioning agents to remove toxic metal ions released in acid soil were prepared by radical-sulfonation and alkaline-oxygen treatment of kraft lignin. Interaction between modified lignins and metal ion (Al^{3+}) was investigated using potentiometric titration. It is well known that proton is released by

coordination of acidic functional groups in organic compounds to metal ion. The coordination bond between lignin and Al was estimated by the change of shape of titration curves. It was suggested that carboxyl and phenolic groups in modified lignins behave as a ligand, because formation of coordinate bond was clearly observed in the complex of Al and modified lignin by only alkaline-oxygen treatment.

1997-P22

Daphne odora におけるリグナン生合成について

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Lignan biosynthesis in *Daphne odora*

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Abstract: (-)-Pinoresinol and (+)-matairesinol were isolated from *Daphne odora*. These lignans were (almost) optically pure. In addition, lariciresinol, secoisolariciresinol and isolariciresinol were detected by GC-MS. [9,9-^{2}H2, OC^{2}H3]Coniferyl alcohol was administered to this plant, and incorporation of deuterium atoms into several lignans were observed. The results suggested that the step to produce optically pure lignan is the formation of pinoresinol from coniferyl alcohol in *D. odora*.

1997-P23

8-*O*-4’型ネオリグナンの *Fusarium solani* M-13-1 による変換（第 2 報）

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Transformation of 8-*O*-4' neolignans by *Fusarium solani* M-13-1, II.

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Abstract: $\Delta^{8'}$-4,7-Dihydroxy-3,3’-dimethoxy-8-*O*-4’-neolignan was prepared by incubation of intact *Fusarlium solani* M-13-1 cells with (±)- $\Delta^{8'}$-4-hydroxy-3,3'-dimethoxy-7-oxo-8-*O*-4'- neolignan in the presence of α-oxo-guaiacylglycerol-β-vanilfin ether. The neolignan obtained was a mixture of (-)-*erythro* and (+)-*threo* isomers, which were enantiomerically pure. Their absolute configuration were determined with the modified Mosher's method as (7*S*, 8*R*)-(-)-*erythro* and (7*S*,8*S*)-(+)-*threo*, which would be derived from both enantiomers of the racemic substrate. This fungal reduction seems to be highly enantioselective but of low substrate specificity, indicating that this reduction could be applied to preparation of other 8-*O*-4' neolignans.

第 43 回 （1998.10.26-27）府中グリーンプラザ

1998-101
グニンの水酸基の新しい定量法
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The new method for the quantitative determination of the hydroxyl groups in lignins
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Abstract: Lignins have aliphatic hydroxy groups at C-γand C-α positions on the side chain in addition to phenolic hydroxy group at C-4 position of aromatic ring. The chemical and physical properties of lignin are almost determined by these hydroxy groups. Therefore, it is very important to determine these hydroxy group contents in lignins. Several methods for quantitative determination of three hydroxy groups in lignins have been reported. Here, we propose a new method for the quantitative analysis of these three hydroxyl groups.

1998-102
酢酸リグニンの性質及び利用
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北海道大学農学部
Characterization and utilization of acetic acid lignins: Methylolation of lignin and preparation of lignin-based adhesives
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Abstract: Acetic acid lignins from rice straw (R-AcL), birch (B-AcL) and fir (F-AcL) were methylolated by three routes: direct methylolation with formaldehyde, condensation with phenol formaldehyde resins and methylolation after phenolization. By the third route, as many as 6-8% methylol groups could be introduced into the lignins. Thermo-setting adhesive with acceptable bonding strength was made from F-AcL in a ratio of 2: 1 (lignin to phenol). Cold-setting adhesives were also prepared with satisfactory bonding quality from both F-AcL and B-AcL in a proportion of 2 : 1 : 1.2 (lignin/phenol/resorcinol).

1998-103
ケナフ靭皮繊維からの高粘度溶解用パルプの調製法
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高知大学農学部
Pulping method of kenaf bast fiber for high viscosity pulp
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Abstract: In order to obtain high viscosity pulp from kenaf bast, a combination of Amox pretreatment, soda pulping under normal pressure and chlorite bleaching is found the most suitable method. The pulp viscosity did not directly correlate to the fiber length or the carbohydrate composition of kenaf bast pulp, but it rather depends on the treatment history of the pulping.

1998-104
酸素漂白過程における酸化反応の解析
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東京大学大学院農学生命科学研究科
Quantitative analysis of oxidation reaction during oxygen-alkali bleaching
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Abstract: Residual lignin and residual hemicellulose were isolated from unbleached softwood kraft pulp. They were separately or as a mixture, subjected to alkali treatment with or without oxygen, and the change in the permanganate consumption during the treatment was analyzed. The permanganate consumption by the isolated residual lignin decreased to about one third of the initial value by prolonged oxygen alkali treatment whereas it changed only to a minor extent when oxygen was absent. Contrary to this, permanganate consumption by the isolated residual hemicellulose increased significantly during the alkali treatment without regard to the presence of oxygen. This result indicates that new structures, which consume permanganate, are produced from hemicellulose even during a weak alkali treatment such as oxygen bleaching and these can not be oxidized by oxygen. By taking those into account, the progress and the extent of the lignin oxidation during oxygen-alkali bleaching of kraft pulp was reevaluated.

1998-105

リグニンのオゾン酸化過程で生じるラジカル反応の抑制

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Suppression of radical reaction caused during ozonation of lignin

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Abstract: Ozone reacts with lignin through two pathways. One is an ionic reaction which generates muconic acid derivatives and hydrogen peroxide. The other one is a radical reaction. The first step of which is the one electron oxidation of dissociated phenolic OH and thus the radical chain reactions are initiated. To control the initiation of radical reactions which brings about the non-selectivity of ozone reactions, ozonation was performed at quite low pH for the purpose of suppressing the disocciation of phenolic OH. The result showed that even at pH 0.7, the amount of hydrogen peroxide formed by the ionic reactions was 1 mmol more for veratryl alcohol (non-phenolic) than that for vanillyl alcohol (phenolic). To explain the difference in the yield of hydrogen peroxide, we have investigated the H2O2-stabilizing effect of MeOH since a doublet amount of MeOH was formed from veratryl alcohol and MeOH is known as a radical scavenger. Furthermore, hydrogen peroxide is also formed by the reaction of MeOH with ozone. But, both possibilities were neglected.

1998-106

リグニン立体構造の解析を目的としたオゾン分解法の定量性の検討

秋山拓也、松本雄二、飯塚堯介

東京大学大学院農学生命科学研究科

Investigation of lignin stereo structure by ozonation

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Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Ozonation method as an analytical tool of stereo-structure of lignin was reexamined by the use of a lignin model compound veratrylglycerol-β-guaiacyl ether (VG). The yield of erythronic and threonic acids from VG was found to be 58%, which was higher than that formerly reported. Prolonged ozonation (20 min to 120 min) did not result in a significant yield loss of these products. Contrary to this, when erythronic and threonic acid in their free acid form were subjected to ozone treatment, their recovery decreased with prolonged reaction time. However, if the reaction mixture were reduced by sodium thiosulfate, their recovery was improved. *Erythro* and *threo* ratio of VG determined based on the yield of ephronic acid and threonic acid was slightly higher than the ratio determined by ^{1}H-NMR. Reproducibility of the GC determination of the products was quite satisfactory when ozonation products were trimethylsililated from their ammonium salts by a mixture of HMDS and TMSCl in DMSO.

1998-特別講演 I.

The challenges and opportunities of lignin

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Abstract: Lignin comprises approximately 1/4 of the earth's biomass production of estimated 10^{10} tops per year. In the process of pulp and paper production, approximately one ton of lignin is separated from biomass for each two tons of paper produced. This means that approximately 100 million tons of lignin are commercially separated from biomass annually worldwide. Only about one percent of that amount is actually recovered from spent pulping liquors for commercial, non-fuel uses. Virtually all of the approximately one million tons of lignin co-generated from pulp and paper operations in the world annually are marketed as water-soluble lignin sulfonate derivatives (Table I). The worldwide value of this market is estimated to be $600 million per year (1). Lignosulfonates have captured the majority of the industrial ionic surfactant markets owing to their favorable price/performance relationship. Prominent uses are in concrete admixtures, animal feed, oil well drilling muds, and dust control agents. Having satisfied major commodity markets, lignosulfonate producers are now focusing on markets for specialty water-soluble polymers. Since the majority of lignin is separated from biomass in

non-sulfonated form, as water- insoluble polymer, the potential exists for lignin to become a competitor in the market for structural polymers, adhesives, and composites. The use of lignin in thermosets and thermoplastics requires a significant level of understanding regarding the structure-property relationships of the polymeric resource. This understanding concerns in particular (a) the chemistry of the basic repeat unit structure(s); (b) the nature of the intermonomer bonds; (c) the size and weight distributions of the molecular mixture; and (d) aspects of the inter/intramolecular interactions. This paper deals with a review of the current state-of-art of the quantitative analysis of lignin's chemical and molecular structure, and on techniques qualified to characterize the performance of lignin in thermosetting resins and in melt-processed thermoplastics.

1998 特別講演 II.
リグニン利用の現状と将来展望
町原　晃
日本製紙株式会社
The current usage of lignin and its prospects
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Abstract: Currently, industry utilizes lignosulfonate (obtained from sulfite liquor) and kraft lignin (extracted from kraft black liquor). Demand for lignin products are increasing in the field such as concrete admixtures and dye dispersants. In order to enhance the usefulness of lignin, it is essential that the features of lignin should be characterized and the original properties must be improved to

be the value added products and the mass consumption. Also, it is necessary in future to solve technical problems, explore new applications and continually develop the values of lignin.

1998-201
Kapok 繊維の油吸着特性と繊維の化学的・組織学的性状
堀　啓映子[*1]、Maxima E. Flavier[*2]、空閑重則[*1]、飯山賢治[*3]
[*1] 東京大学大学院農学生命科学研究科、[*2] フィリピン大学化学研研究所、[*3] 東大アジア生物資源環境研究センター
An excellent oil absorbent, Kapok (*Ceiba pentandra* (L.) Gaertn.) fibre: its fibre structural and chemical characteristics
Keko Hori[*1], Maxima E. Flavier[*2], shigenori Kuga[*1],OKenji Iiyama[*3]
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1998-202
リグニンと古紙を原料とする成形活性炭の吸着性能
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Adsorption property of molded activated carbon prepared from lignin and waste paper
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Abstract: The activated carbon (AC) with sheet shape (ACS) which was a new type of molded AC was prepared from the mixture of isolated lignins and waste news paper. The adsorption capacities of ACSs were higher than those of commercial powdery and granulated ACs. Particularly, ACSs prepared from acetic acid lignin (AL) showed the excellent adsorption capacity: iodine 1,350 mg/g; metylene blue 225 mg/g and *p*-chlorophenol 1,250 mg/g, resectively. Furthermore, *p*-chlorophenol adsorption rate of AL-ACSs was faster than that of the commercially granulaced activated carbon. These results revealed that AL was an effective material for molded activated carbon. The ratio of internal surface to external surface area of AL-ACSs from nitrogen sorption was much higher than that of commercial powdery AC, suggesting that the excellent adsorption capacity of AL ACS was based on development of meso- and micro-pores which acts as adsorption sites.

1998-203
ヒドロキシプロピル化リグノセルロースの性質
半崎亜希子、浦木康光、佐野嘉拓

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Characteristics of hydroxypropylated lignocellulose

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Abstract; Hydrophobically associating water-soluble polymers (HAWSP) have been focused on their unique theological properties and the functions as inclusion compounds for drugs and proteins. HAWSP was prepared from acetic acid pulp (AWP) by hydroxypropylation. The association of hydroxypropylated AWP (HP-AWP) was found to occur in water, and even in chloroform by TEM observation and viscometric measurement. The interactions between HP-AWP molecules in water and in organic solvent seemed to be due to the hydrophobic interaction of residual lignin and to hydrogen bonding of polysacchahdes, respectively. HP-AWP was suggested to have an excellent complexation ability to low molecular-mass compounds. With respect to the interaction with biopolymer, HP-AWP was also indicated to play a role as a stabilizer that prevented protease (papain) from its autolysis.

1998-204

リグニン及びリグニン関連型フェノールを原料とするエポキシ樹脂の調製と熱的性質

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[*1] 福井工業大学工学部, [*2] 物質工学研究所、[*3] 大妻女子大学家政学部

Preparation and thermal properties of epoxy resins derived from lignin and lignin-related phenol

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[*1]Fukui University of Teclmology, [*2]National Institute of Materials and Chemical Research, [*3]Otsuma Women's University

Abstract: Epoxy prepolymers were synthesized from alcoholysis lignin (AL), and lignin-related phenols such as *p*-hydroquinone and methoxy-*p*-hydroquinone by reaction with epichlorohydrin.

Epoxy resins were synthesized from the above prepolymers by reaction with poly(azelaic anhydride). The molar ratios of acid anhydride groups to epoxy groups ([AA]/[EPOXY] ratios) were varied at 10/10 and 12/10. The thermal properties of the obtained prepolymers and epoxy resins were studied by differential scanning calorimetry (DSC), thermogravimetry (TG) and TG-Fourier transform infrared spectroscopy (FTIR). Glass transition temperatures (T_g's) increased with increasing [AA]/[EPOXY] ratios. Thermal degradation temperatures (T_d'S) of epoxy resins were almost constant regardless of [AA]/[EPOXY] ratios, suggesting that the curing of prepolymers with poly(azelaic anhydride) does not affect T_d Values. The intensities of absorption peaks at 2900 cm^{-1} (CH) and 1730 cm^{-1} (C=O) in IR spectra of the evolved gases during thermal degradation increases with increasing [AA/[EPOY] ratios.

1998-205

分子状酸素によるアルデイトール類の直接酸化

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Direct oxidation of alditols by molecular oxygen

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Abstract: Alditols can be easily oxidized by oxygen-alkali treatment without any active oxygen generator such as a phenolic compound. When alditol (xylitol, D-arabinitol or ribitol) was treated at 95ºC, the oxidation was quite rapid and no induction period seemed to be present until the oxidation started. However, when the reaction was carried out at 55ºC or 70ºC, the presence of induction period was clearly observed. The induction period at these temperatures increased when a small amount of a known stabilizer of peroxides (diethylenetriaminepentamethylene-phosphonic acid, DTMPA) was added to the reaction system. These observations suggest that the oxidation of alditols during oxygen-alkali treatment proceeds by an auto-oxidation type reaction, which consists of an initiation reaction (direct reaction of alditols and molecular oxygen) and the following chain oxidation type reaction. The fact that the addition of DTMPA did not result in a visualization of induction period at 95ºC seems to indicate that the direct reaction with molecular oxygen is much more important in the oxidation of alditols at this temperature than at lower temperature, but no direct proof for this was obtained.

1998-206

リグニンの熱分解：グァイアシルグリセロールおよびコニフェリルアルコール末端基由来の熱分解生成物

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Analytical pyrolysis of lignin: pyrolysis products derived from guaiacylglycerol moieties and coniferyl alcohol-end groups

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Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: Pyrolysis products of acetylated lignin model compounds and reference lignins were analyzed to determine guaiacylglycerol moieties and coniferyl alcohol-end groups. Guaiacylglycerol-β-coniferyl ether tetraacetate produced 3-(4-hydroxy-3-methoxy-phenyl)- propyl acetate **1**, 3-(4-acetyloxy-3-methoxyphenyl)-propyl acetate **2**, and 3-(4-acetyloxy-3- methoxyphenyl)-prop-2-enyl acetate **3**. Guaiacylglycerol-β-guaiacyl ether triacetate produced **2** and **3**. These findings suggested that **1** is indicative for coniferyl alcohol-end groups, and **2** and **3** for guaiacylglycerol moieties. Acetates of reference lignins, synthetic lignins, Japanese cedar wood, its dioxane lignin, and Japanese Douglas fir wood, also produced **1**-**3**. Large differences in yields of **1**-**3** were observed among the acetylated lignins. Pyrolysis using acetylated samples is effective for analyzing guaiacylglycerol moieties and coniferyl alcohol-end groups in lignins.

1998-207

熱分解ガスクロマトグラフィーによるユーカリ中のリグニンの樹幹内変異の解析

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Characterization of within-tree variation of lignin in *Eucalyptus camaldulensis* by pyrolysis-gas chromatography

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Abstract: Pyrolysis-gas chromatography (Py-GC) using a vertical micro furnace pyrolyzer was applied to the detailed estimation of “the within-tree variation” of the ratio of syringyl and guaiacyl units (S/G ratio) for lignin in *Eucalyptus camaldulensis*. On the pyrogram of the *Eucalyptus* obtained at 450ºC, many characteristic peaks derived from syringyl and guaiacyl units of lignin were reproducibly observed together with those from cellulose and hemicellulose. On the basis of the intensities of these characteristic peaks, "the within-tree variation" of the S/G ratio for lignin were estimated rapidly using □g order of the powdered tree sample, and the obtained results were also discussed comparing with those obtained by the thioacidolysis method.

1998-208

コーヒー酸の酸化的二分子縮合における反応機構の考察

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Reaction mechanism of oxidative bimolecular condensation of caffeic acid

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Abstract: We examined a formation of furofuran-type lignan 2,6-*exo*-bis(3,4-dihydroxyphenyl)-3,7-dioxabicyclo[3.3.0]octane-4,8-dione (**4**) from 3,4-dihydroxycinnamic acid (caffeic acid, **1**) with NaIO4, as a model of bimolecular condensation. The first step of bimolecular condensation was thought as the oxidation of **1** to highly reactive *o*-quinone (**3**). It was confirmed by NMR analysis and the reaction of **3** in MeOH with 1,2-phenylenediamine to produce phenazine derivative. Further labeling studies by using [8-^{13}C] **1** revealed that the condensation occurred between **1** and **3**.

1998-209

クロマツあて材リグニンの形成と構造

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Formation and structure of lignin in the compression wood of *Pinus thunbergii*

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Abstract: Lignin is considered to be different in coupling type of its component according to a kind of cell

or a position of cell wall. In this study, we analyzed lignin by thioacidolysis at the level of monomer or dimer. We prepared 50 mm-thick tangential sections (cambial zone to mature xylem) from compression or normal wood of *Pinus thunbergii*, and analyzed how lignin deposit in the process of cell wall differentiation in secondary xylem. By the dimer analysis, heterogeneity of the inter units linkage in lignin was suggested.

1998-210
The behaviors of deuterium labeled monolignols and monolignol glucoside in lignin biosynthesis
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名古屋大学農学部
Fang Chen, Kazuhiko Fukushima, Seiichi Yasuda
Faculty of Agriculture, Nagoya University

Abstract: To examine the different behavior of monolignol and monolignol glucoside in lignin biosynthesis, pentadeutero[γ, γ,-D_2,OMe-D_3]-coniferyl alcohol and pentadeutero[γ,γ-D_2, OMe-D_3]-coniferin were synthesized and fed to growing trees. The difference in patterns of incorporation of labeled precursors was studied by GC-MS. The results indicate that both precursors can be incorporated into lignin effectively, but the labeled coniferyl alcohol can be incorporated into lignin more directly, resulting high proportion of 5D-labeled guaiacyl and syringyl units in newly formed xylem. On the other hand, labeled coniferin tends to be incorporated into 4D-labeled guaiacyl and syringyl units, releasing oneγ-deuterium atom due to oxidation.

1998-211
In situ hybridization 法によるリグニン生合成関連遺伝子の発現解析
島田武明[*1]、川合伸也[*2]、諸星紀幸[*1]
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Expression analysis of lignin-biosynthesis related genes with *in situ* hybridization
Takeaki Shimada[*1], Shinya Kawai[*2], Noriyuki Morohoshi[*1]
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Abstract: We have attempted to construct the experimental system of *in situ* hybridization to detect the expression of lignin-biosynthesis related genes in, *Populus kitakamiensis*, hybrid aspen. *In situ* hybridization is widely employed to analyze tissue-specific gene expressions in both plants and animals. With this method, the analysis of tissue-specific gene expression can be achieved in very short tern, comparing to other methods such as promoter-GUS assay and so on. In the this report, we used one year old stems of *P. kitakamiensis* and detected the *pal* expression in several phloem cells locating cambial zone nearby. This result partially coincided with that of promoter-GUS assay which was conducted formerly. Although *pal* expression was detected, now ye are thinking the signal was not intact, therefore further study is necessary to decide the strict localization of *pal* mRNA and also the identification of isozymes.

1998-212
ダイオキシン分解菌 V2 からのリグニンペルオキシダーゼによるダイベンゾフランの分解
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Degradation of 2,4,8-trichlorodibenzofuran by lignin peroxidase produced by fungus V2 having ability for degradation of dioxins
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Abstract: The time-course of the activities of lignin peroxidase (Lip) and dioxygenase from fungus V2 separated by a screening from natural world and a wood-rotting fungus *Phanerochaete chrysosporium* having ability for degradation of dioxins (2,7-Dichlorodibenzo-*p*-dioxin) was measured in connection with the degradation rate of 2.4.8-Trichlorodibenzofuran (2,4,8-TCDF) with two fungi. We tried to isolate Lip by fungus V2 separated by the screening method. Three Lip fractions were purifled by DEAE-BioGel A. Three Lip fractions (I , II. III) degraded 10.5% to 49.7% of
2,4,8-TCDF. The maximum degradation rate of 2,4,8-TCDF was obtained by Lip fraction II-9 when the incubation was conducted for 3 hours after addition of 0.25 mmol of 2,4.8-TCDF to the fraction. The activity of Lip from fungus V2 was higher in the initial stage of the culture. the degradation rate of 2.4.8-TCDF was larger. The activity of Lip from fungus V2 was decreased with the incubation time. the activity kept a constant level after the incubation for 15 days. However, the degradation rate of 2,4.8-TCDF was increased after the

incubation for 15 days. The degradation rate of 2,4,8-TCDF was increased with the increase in the activity of dioxigenase from fungus V2. The activity of dioxygenase from fungus V2 was higher, the degradation rate of 2,4,8-TCDF was larger. These results suggested the participation of both Lip and dioxygenase in degradation of 2.4.8-TCDF.

1998-213

白色腐朽菌のリグニン分解に関与する脂質過酸化に関する研究

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Studies on lipid peroxidation during lignin degradation by white-rot fungi

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Abstract: White-rot fungus *Coriporiopsis subvermispora* is known to decompose cell wall lignin without morphological changes of wood cell walls. Since enzymes cannot penetrate inside of the wood cell walls during this stage, this reaction must be catalyzed by low molecular mass compounds. To elucidate the selective ligninolytic system, we focused on extracellular peroxidizable compounds such as lipid since the peroxidizable compounds can generate active radicals inside of wood cell walls even at the site far from enzymes. Analysis of peroxidizable compounds prduced by *C. subvermispora* is reported.

1998-214

化学修飾法を用いたリグニンペルオキシダーゼ基質酸化機構の解析

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Spectroscopic and kinetic characterization of chemically modified lignin peroxidase

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Abstract: To investigate a reaction mechanism, chemically modified lignin peroxidases were prepared using N-bromosuccinimide (Lip-NBS) and 1-ethyl-3-(3-dimethylaminopropyl)-carbo- diimide with and without 2-aminoethanesulfonic acid (S- and EDC-LiP). Reactivity of LiP against veratryl alcohol (VA), 2,6-dimethoxyphenol, and ferrocytochrome *c* was remarkably reduced by the chemical modification. On the other hand, reactivity against 2,2’-azinobis-(3-ethylbenzthiazoline- 6-sulfonate), KI, and ferrocyanide was almost unchanged upon the modification. This observation strongly suggests that LiP may have two or more substrate oxidation sites. To further characterize the mechanism, steady state kinetic parameters of modified LiPs on VA oxidation were determined, indicating that the NBS modification reduces all electron transfer efficiency rather than a substrate binding. The effects of the chemical modification on the role of VA in LiP oxidation of ferricyto- chrome *c* were determined. The extents of the inhibition by the chemical modification using NBS and EDC against VA oxidation and VA-supported oxidation of ferricytochrome *c* were very similar, suggesting that VA binding sites may be the same when acting as a reducing substrate and as a cofactor during ferricytochrome *c* oxidation.

1998-215

デンドリティツクポルフイリンの触媒するペルオキシダーゼ型反応

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Dendritic porphyrin designed for eatalyzing peroxidative reaction

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Abstract: Lignin peroxidase (LiP) oxidizes a variety of nonphenolic aromatic compounds including chlorinated dibenzo-*p*-dioxins and biphenyls to their aryl cation radicals. To maximize LiP-catalyzing oxidation of those pollutants, a stable one electron oxidation activity in organic media has been expected. Using an iron-*meso*-tetra(4-carboxyphenyl)porphine as a core, which has higher redox potential than the iron-protoporphyrin IX, the dendritic porphyrin was synthesized to mimic LiP catalysis. The relationships

between the size of dendron (generation 1 (G1) to G4) and LiP activity, peroxide-derived inactivation, and kinetic characteristics were examined. G4-dendritic porphyrin shows a stable one-electron oxidation activity in organic media via a typical peroxidase catalytic cycle. The addition of imidazole derivatives improved either LiP or peroxidase activity of G4-dendritic porphyrin.

1998-216

白色腐朽菌によるポリエチレンの分解（IV）—過酸化水素非存在下での MnP による Mn(III)の生成機構—

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Polyethylene degradation by white-rot fungi (IV), -Formation of Mn(III) by MnP in the absence of hydrogen peroxide

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Abstract: We have investigated the degradation of high-molecular-weight polyethylene membrane by (MnP). The previous study clearly indicated that Mn(III) formed by MnP function closely relates to the polyethylene degradation in the absence of hydrogen peroxide. We, therefore, studied the mechanism for formation of Mn(III) by MnP without hydrogen peroxide supply during polyethylene degradation. The Mn(III) formation was completely inhibited under nitrogen atmosphere and was accelerated by addition of Mn(III) or Mn(IV) in the reaction system. The effect of the Mn(III)-addition was also restrained under nitrogen atmosphere. These results indicate that the reaction of oxygen, Mn(III), and MnP initiates the MnP catalytic cycle. The peroxidation of unsaturated lipid did not participate in the formation of Mn(III) by MnP nor polyethylene degradation in the our system.

1998-217

Phanerochaete sordida YK-624 株のマンガンペルオキシダーゼ遺伝子について

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Manganese peroxidase genes from the white-rot fungus *Phanerochaete sordida* YK-624

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Abstract: We have cloned and sequenced the *mnp* genes encoding isoenzymes of manganese peroxidase (MnP) from the white-rot fungus *Phanenochaete sordida* YK-624 under nitrogen-limiting condition. At least four *mnp* cDNAs were cloned. The predicted amino-acid sequence of these isozymes showed a high degree of identity each other and also highly conserved to MnP families of other white-rot fungi.

1998-218

1−HBT 存在下における非フェノール性 β-O-4 型ジリグノールのカワラタケラッカーゼによる芳香環開裂

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Aromatic ring cleavage of nonphenolic β-O-4 dilignol by laccase of *Coriolus versicolor* in the presence of 1-HBT

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Abstract: Aromatic ring cleavage products, 1-(4-ethoxy-3-methoxyphenyl)glycerol-γ-formyl ester and 1-(4-ethoxy-3-methoxyphenyl)glycerol-β,γ-cyclic carbonate, were idendfied as degradation prodcuts of nonphenolic β-*O*-4 lignin substructure model compound, 1,3-dihydroxy-2-(2,6-dimethoxylphenoxy)-1-(4-ethoxy-3-methoxyphenyl)propane, by a *Coriolus versicolor* laccase in the presence of 1-hydroxybenzotriazole.

1998-219

非水媒体中で機能する界面活性剤　—ラッカーゼ複合体—

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Surfactant-laccase complex catalytically active in anhydrous media

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Abstract: A surfactant-laccase complex was prepared with a nonionic surfactant utilizing water-in-oil emulsions. The complex was easily soluble in anhydrous toluene and effectively catalyzed the oxidation of *o*-PDA in such bitterly harsh environment. In contrast, lyophilized laccase hardly catalyzed the reaction process. The preparation and reaction conditions of the complex have been optimized through studies of the effect of aqueous pH in the W/O emulsions, surfactant concentration, enzyme concentration at preparation stage, and the nature of the organic solvents.

1998-P01

カワラタケの Hsp30 の遺伝子解析

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Gene analysis of HSP30 from *Coriolus versicolor*

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Abstract: White-rot fungus *Coriolus velsicolor*, a ligninolytic basidomycete, has been studied because of its ability to degrade hazarous chemicals. In this study, two genomic DNAs coding for the Hsp30 were isolated from *C. versicolor*. The nucleotide sequences of the two genes differ by 37 base changes within the open reading frames resulting in 3 amino acid substitutions. Three small introns interrupt genomic DNAs. Putative eukaryotic regulatory sequences, CAAT-box and TATA-box, are exist in the promoter regions. The regions contain the consensus heat shock element, xenobiotics response element and metal response element sequences. Northern blot hybridization indicate that the expression of the Hsp30 gene is constitutive at a normal temperature and is accelerated at elevated temperature. That expression level is higher in *C. versicolor* cells that has been exposed to pentachlorophenol.

1998-P02

MnP バイオブリーチングにおける Tween 80 の役割

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The role of Tween 80 in biobleaching with manganese peroxidase

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Abstract: The role of Tween 80 in biobleaching of hardwood kraft pulp (HWKP) with manganese peroxidase (MnP) was investigated. The most increase of pulp brightness was obtained with Tween 80 among the surfactants, Tween 80, Tween 20, and CHAPSO. The MnP activity assayed in the presence of each surfactant was similarly increased by approximately 1.5 times that of control (no surfactants). Tween 80 had less stabilizing effect on MnP than other surfactants during MnP- biobleaching. Lipid peroxidation of Tween80 during MnP-biobleaching by TBA methods was not noticeable. Neither these characteristics of Tween 80 nor delignification by the radical derived from the lipid peroxidation did not explain the most appreciable effect on the brightness increase by Tween 80.

1998-P03

マンガンを除去した各種クラフトパルプのバイオブリーチング

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Biobleaching of various kraft pulps removed manganese by EDTA

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Abstract: When EDTA-extracted oxygen-bleached hardwood kraft pulp (EDTA-extracted LOKP) was bleached with *Phanerochaete sordida* YK-624, brightness was increased without secretion of manganese peroxidase. In order to clarify this phenomenon, various kraft pulps delignified with chlorine compounds and xylanase were treated with the fungus. When EDTA-extracted oxygen- bleached softwood kraft pulp delignified with chlorine dioxide was treated, the brightness was not increased. When EDTA-extracted unbleached

hardwood kraft pulp delignified with chlorine and chlorine dioxide was treated, both pulps were not bleached. Effect of xylanase on biological bleaching of EDTA-extracted LOKP was not observed. Consequently, only EDTA-extracted LOKP was bleached.

1998-P04

シロアリによるリグニンの分解（II）—イエシロアリによる高分子リグニンの分解—

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Degradation of lignin by termites (II), - Degradation of synthetic lignin by *Coptotermes formosanus*

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Abstract: We examined the degradation of lignin (DHPs) by termite *Coptotermes formosanus*. For 1 week treatment by *C. formosanus*, DHP combined with 4-methylumbelliferone was hardly degradaed, and the low-molecular-weight fraction of the DHP was polymerized. ^{13}C-NMR spectrum of β-^{13}C-DHP treated by *C. formosanus* for 12 days suggests that *C. formosanus* unselectively degraded DHP.

1998-P05

広葉樹培養細胞のリグニン生合成における前駆体投与の影響

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The effect of lignin precursors feeding on lignin biosynthesis in *Populus* calluses

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Abstract: Precursors of lignin, ferulic acid (FA) and sinapic acid (SA), were administered to poplar (*Populus alba* L.) callus cultures. FA and SA addition induces increased levels of lignin in poplar calluses. Alkaline treatment of cell wall followed by determination of FA and SA from cell walls and alkaline nitrobenzene oxidation suggest that administered FA is incorporated into both guaiacyl and syringyl lignins, while SA into only syringyl lignin. A marked increase in 4-Coumarate:CoA ligase (4CL) activity against FA was not observed in the calluses cultured with FA-addition. The increased 4CL activity against SA was correlated with the increase in syringyl lignin composition in FA or SA administered calluses. The other class of 4CL which utilizes SA may be induced in poplar calluses by an extraordinarily high level of FA or SA in calluses.

1998-P06

Anthriscus sylvestris のリグナンの生合成について

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Lignan biosynthesis in *Anthriscus sylvestris* Hoffm

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Abstract: L-[Ring-^{13}C6]phenylalanine and [9,9-^{2}H2, OC^{2}H3]coniferyl alcohol were incorporated into secoisolariciresinol and yatein in *Anthriscus sylvestris* Hoffm. (Umbelliferae). Furthermore, cell-free extracts from the leaves of *A. sylvestris* catalyzed the enantioselective formation of (+)-lariciresinol and (+secoisolariciresinol from (±)-pinoresinols in the presence of NADPH. The enantiomeric compositions of the lignans formed by the cell-free extracts show the similarity to that in case of *Forsythia* enzyme preparations.

1998-P07

Linum flavum var. compactum から単離された新規ジベンジルブチロラクトンリグナンについて

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A new dibenzylbutyrolactone lignan from *L.inum flavum* var. *compactum*

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Abstract: A new dibenzylbutyrolactone lignan 7, 6'-dihydroxybursehernin was isolated from the methanol extracts of *L.inum flavum* var. *compactum* which is known to contain an antitumor lignan methoxypodophyllotoxin. 7, 6'-Dihydroxybursehernin was a unique dibenzylbutyrolactone lignan having 3’, 4'-methylenedioxy-6'-hydroxy phenyl group.

1998-P08

ネジキにおけるシリンギルリグナン生合成の初期反応について

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Initial reactions in syringyl lignan biosynthesis in *Lyonia ovalifolia* var. *elliptica*

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Abstract: *Lyonia ovalifolia* var. *elliptica* contains (+)-lyoniresinol (LYR) which is a syringyl and aryltetrahydronaphthalene lignan. To investigate biosynthesis of (+)-LYR and the related syringyl lignans, feeding experiments of radio-isotopically labeled precursors to excised shoots of the plant were performed. It was found that [8-^{14}C]sinapyl alcohol was incorporated into (+)-[^{14}C]5,5'- dimethoxylariciresinol (DMLAR) and its glycosides, and (+)-[^{14}C]LYR glycosides, but not into [^{14}C]5,5'-dimethoxysecoisolariciresinol. The result suggested that an enantiospecific reduction of syringaresjnol gave (+)-DMLAR which was then converted to (+)-LYR.

1998-P09

熱分解—質量分析（Py-MS）および多変量解析による草本類リグニンの分析

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Analysis of herbaceous lignins by pyrolysis-mass spectrometry (Py-MS) and multivariate analysis

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Abstract: Several kinds of herbaceous materials were characterized using pyrolysis-mass spectrometry (Py-MS), The mass spectral data were further analyzed by principal component analysis (PCA) and factor analysis (FA) in order to investigate the relationships between pyrolysis products and samples. PCA clearly showed the differences in fractions and growth stages of the samples, quantitative analysis of lignin by Py-MS and FA was examined. The results showed the correlation between acetyl bromide lignin content and factor score of FA.

1998-P10

塩素漂白で生成した高分子有機塩素化合物の環境中での挙動（3）酸化リグニンの熱分解生成物中に見出されるアルカンタイプ構造の起源について

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Environmental fate of high molecular weight chloroorganics produced by chlorine bleaching (III), Origin of alkane type structures detected in pyrolysis products from oxidized lignins

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Abstract: Pyrolysis gas chromatographic analysis showed that alkane type structures were produced as major pyrolysis products of oxidized lignins. Therefore, the authors assumed these structures might originate directly from oxidized aromatic structures of lignin when they underwent pyrolytic decomposition. By the further study, however, we have come to the conclusion that some unknown structures (i.e. extracts from wood) extracted together with lignin from unbleached kraft pulp are the main source of these alkane type structures. We'll also report the structural modification of extract components during bleaching, the knowledge of which is very limited.

1998-P11

FT−Raman 分光法を用いたリグニン S／G 比の非破壊的な定量

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Non-destructive determination of lignin syringyl/guaiacyl monomeric composition in native wood by Fourier transform Raman spectroscopy

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Abstract: The feasibility of using FT-Raman spectroscopy for rapid non-destructive determination of lignin syringyl/guaiacyl (S/G) monomeric composition was examined using *Eucalyptus camaldulensis* and *E. globules*, including samples of various ages and colors, which are of importance as a plantation source. The application of 2nd derivatives transformation of Raman spectroscopic data revealed highly significant correlations between wet chemical and Raman predicted values with correlation coefficient (r) = 0.998 and standard error of prediction (SEP) <0.07 points in the calibration (for known samples), and r=0.935 and SEP<0.32 points in the prediction (for unknown samples) respectively. Consequently, this non-destructive method has proved its validity for analyzing *Eucalyptus* native wood meal samples, regardless of their age and color to determine lignin S/G monomeric composition. Using FT-Raman spectroscopy, elite tree selection based on quality aspects for pulp and paper production can be performed.

1998-P12

マングローブ樹皮タンニンの性状

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Characteristics of tannins from the bark of *Sonneratia caseoralis*

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Abstract: Chemical characteristics of tannin components from the bark of *Sonneratia caseoralis* were investigated. The bark contained 15.9% polyphenols, 4.2% flavanols and 4.9% tannins. From the ethyl acetate extracts of 70% acetone aqueous extracts, gallic acid was isolated. The acetone aqueous extracts from the bark were submitted to both pyrolysis gas chromatography and on-line methylation pyrolysis gas chromatography. Consequently, it has been made clear that pyrogallol and 3,4,5-trimethoxybenzoic acid methyl ester were the main products of pyrolysis gas chromatography and on-line methylation pyrolysis gas chromatography, respectively. These results indicate that the bark of *S. caseoralis* contains condensed tannins with more amounts of pyrogallol-type B-rings in more amounts than with catechol-type B-rings, and that hydrolysable tannins are the main tannin components of *S. caseoralis*.

1998-P13

南洋材含有アントラキノン類の迅速な定量およびチーク材抽出物の蒸解助剤効果

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Rapid analysis of quinones in tropical hardwoods and catalytic effects of teak extract on pulping

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Abstract: Teak (*Tectona grandis*) wood contains 2-methyl anthraquinone (MAQ), which is an effective catalyst for alkaline pulping woods and other lignocellulosics. Pyrolysis-gas chromatography (Py-GC) was found to be a useful method for the rapid determination of MAQ and anthraquinone (AQ) in a very small amount of wood, bark and other samples. Teak heartwood of wood samples from Myanmar was shown to contain 0.47-1.10% MAQ, but not AQ. The sapwood, the bark, and other tropical hardwoods (approximately 20 species) did not contain MAQ at all. The teak wood samples were extracted with some organic solvents. The extract contents were 7.0-9.9%, and the results from GC showed that MAQ was approximately 5% of the extract. Compared with the GC method accompanied by extraction, the Py-GC method is very useful in searching for a plant which contains anthraquinones. Genetic modification of trees to produce MAQ that catalyzes their own pulping is an attractive topic. The alkaline pulping of eucalyptus (*Eucalyptus camaldulensis*) wood was carried out in the presence of 0.6% teak extract (0.06% as MAQ) and of 0.06% synthesized MAQ. The teak extract had better effects on delignification.

1998-P14

酸素–アルカリ漂白過程における多糖類の分解機構（10）

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Degradation mechanisms of carbohydrate during oxygen-alkali bleaching process (X)

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Abstract: A cellulose model compound, methyl β-D-glucopyranoside (MGP) and a non-phenolic lignin model compound, 3,4-dimethoxybenzyl alcohol (veratryl alcohol, VA) or 1-(3,4-dimethoxy-phenyl)-1,2-ethanediol (veratryl glycol, VG), were subjected to oxygen-alkali treatments with 2,4,6-trimethylphenol which was an active oxygen generator in this system.The degradation of VG was much larger than the degradation of VA under high pH. This indicates that the side chain part of lignin model compounds participates in the reaction with active oxygen species more than the aromatic part does under high pH. Reaction selectivity was higher when VG was used as a non-phenolic lignin model compound than when VA was used as that under high pH, but the reverse was the case under low pH.

1998-P15

免疫法によるクラフト蒸解中のグルコマンナンおよびキシランの挙動の可視化

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Visualization of the behaviors of glucomannan and xylan during kraft pulping by immuno- microscopical technique

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The distribution of glucomannan and xylan in pine wood was visualized by immune- microscopy at various stages of kraft pulping to investigate their behaviors during the pulping. Using anti-glucomannan antibody, secondary wall was entirely immuno-labeled in non-kraft treated wood, whereas in kraft treated wood lumen side of secondary wall was labeled preferentially. Using anti-xylan antibody, the lumen side was preferentially immuno- labeled in both non-kraft treated wood and kraft treated wood. These results indicate that during kraft pulping glucomannan and xylan were dissolved in pulping liquor in cell wall, and the hemicelluloses moved to lumen side of cell wall with diffusion of pulping liquor and were concentrated in this side, then eluted from wood.

1998-P16

未利用プランテーションバイオマスの有効利用開発：ココナッツ・コアイアダストからの土壌改良材の調製とその性状

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Effective utilization of plantation waste biomass. -Soil conditioner from coconut coir dust

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Abstract: There are many plantations producing latex, palm oil, coconut oil, sugar, cacao coffee beans, and so on, in tropical region. Huge quantities of waste and residue are produced during harvesting commercial products and replanting. The most of these waste and residues are not effectively utilized yet. It is significant important for conservation of global environmental and sustainable production of biomass to utilize these wastes and residue. In this paper, we focused coconut coir fiber (CCF) and coir dust (CCD) to develop their effective utilization. Chemical composition of these materials were analyzed and its structural feature were characterized. Both CCF and CCD were carboxymetylated to be utilized as soil conditioner. The Cm-CCF and CM-CCD were fractionated into water-soluble and insoluble fractions and characterized their chemical feature. Then their water absorbtivety was examined.

1998-P17

酸リグニンより可溶性アリールリグノスルホン酸および陽イオン交換樹脂の調製

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名古屋大学農学部

Preparations of soluble aryllignosulfonic acid and cation exchange resin from acid lignin

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Abstract: Preparations of soluble aryllignosulfonic acid and cation exchange resin from gymnosperm

sulfuric acid lignin (Klason lignin) (SAL) were tried. Soluble aryllignosulfonic acid was prepared from SAL by sulfuric acid-catalyzed phenolation, chlorosulfonation and final alkali hydrolysis. Reaction mechanism was confirmed in a separate experiment with a model compound. Furthermore, cation exchange resin was prepared by a series of reactions of SAL, that is, resinification with formalin, chlorosulfonation and alkali hydrolysis. Ion exchange capacity of it was 3.2 meq/g.

第44回（1999.10.7-8）岐阜大学農学部

1999-101
スギ胚へのパーティクルガン法による遺伝子導入
田仲徹称、七澤雅治、諸星紀幸
東京農工大学大学院生物システム応用科学研究科
Gene introduction into Sugi embryo with particle bombardment
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Abstract: Lignin is one of the major components in woody plant cell wall. The quantity and quality of lignin have an influence on the pulping and the biomass utilization. In the future, their improvement will be required for utilization of the biomass more effectively. In this study, we tried to regenerate Sugi (*Cryptomeria japonica* D.Don), which is a useful conifer in Japan, and to establish a transformation system of Sugi. We succeeded to introduce foreign genes into Sugi embryo with particle bombardment.

1999-102
細胞壁の木質化に関与する酵素の局在
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Distribution of enzymes involved in lignification of cell wall
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Abstract: One of the most characteristic phenomena in woody plants is lignification of cell walls. Almost all of the enzymes involved in lignification are now well known. However, much more works are needed to elucidate the localization of these enzymes in the cell, relation of enzymes to cell differentiation, and regulatory mechanism of synthesis of these enzymes. We applied the immuno- cytochemistry by using the antibodies against the enzymes involved in lignification, and showed the enzymes involved in biosynthesis of monolignols are synthesized at polysomes and then are dispersed into the cytosol of the lignifying cells. Therefore, monolignols are synthesized in the cytosol and transported to the cell wall by passing through the plasma membrane. On the contrary, the enzyme involved in dehydrogenative polymerization of monolignols is synthesized in rough endoplasmic reticulum and transported to lignifying cell walls via the Golgi apparatus. Finally lignification occurs in the cell walls.

1999-103
ケナフ（*Hibiscus cannabinus*）靭皮、コア及び根の細胞壁成分の生長にともなう変化と光合成能
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Core and root of maturing kenaf (*Hibiscus cannabinus*).
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1999-104
リグニン化学構造の不均一性（3）—TMSiI を用いたエンドワイズリグニンの評価—
掘啓映子、飯塚堯介
東京大学大学院農学生命科学研究科
Structural heterogeneity of hardwood lignjn (III), - Estimation of endwise lignin fraction by TMSil treatment
Keko Hori, Gyosuke Meshitsuka
Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Endwise lignin fraction, was composed mostly of syringyl units and β-*O*-4 intermonomer linkages, was found in birch periodate lignin. The endwise lignin fraction should be cleaved to monomer by TMSiI (trimethylsilyl iodide) under a very mild condition. Sinapyl alcohol was the main peak of GC chromatogram after TMSiI treatment for 3hr, but the yield was not very high. Syringylpropane monoiodide was detected by GC analysis after 72hr TMSiI treatment, but the peak was not detected after Zn treatment. The molecular weight distribution after Zn treatment is now under investigation.

1999-105
リグニンの三次元構造の推定方法に関する考察
寺島典二
名古屋大学
Possible approaches for estimating three dimensional structure of lignin
Noritsugu Terashima
Nagoya University

Abstract: Lignin structural models proposed in the past provide information insufficient to predict chemical behavior of lignin in the cell wall. An advanced 3D structural model should contain information on structural heterogeneities and macromolecular properties as follows; (I) distribution and frequencies of different kinds of units, functional groups, inter-unit bonds, lignin-polysaccharide bonds in lignin macromolecule and in the cell walls, (2) higher order structure and size of lignin macromolecule, and (3) 3D assembly of lignin and polysaccharides in different morphological regions of cell walls and in different kinds of cells. Based on the information obtained by non-destructive analyses employing improved radio- and stable isotope tracer methods combined with the information by electron microscopy and other various destructive analyses, a 3D model can be proposed tentatively. For further revision of the model, improvements of the approaches to get more reliable information especially on (3) are required.

1999-106
TOF−SIMS イメージによるリグニン構造解析の試み
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Analysis of lignin structure by TOF-SIMS
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[*1]Graduate School of Bioagricultural Sciences, Nagoya University, [*2]ULVAC-PHI. Inc.

Abstract: The structure of lignin of tree xylem was investigated by TOF-SIMS. Pine and beech MWLs gave some secondary ions which had guaiacyl or syringyl nuclei on TOF-SIMS analysis. Deuterium labeled magnolia xylem fed with phenylalanine-d7 gave the image which represent the localization of deuterium on the surface of xylem on TOF-SIMS analysis.

1999-107
リグニンの熱分解：β−5 型構造由来の熱分解生成物
黒田健一
筑波大学農林工学系
Analytical pyrolysis of lignin: pyrolysis products derived from the β-5 building blocks
Ken-ichi Kuroda
Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: Dehydrodiconiferyl alcohol and its related compounds **II-V** were pyrolyzed at 500ºC for 4s. The predominance of 4-methylguaiacol (a 27 % (mol/mol) yield from **I**) was observed in the monomeric products, suggesting that in pyrolysis of lignins parts of 4-methylguaiacol are derived from the β-5 building blocks. Pyrolysis product profile of **I** methylated by diazomethane showed that the products derived from the β-5 building blocks are extensively derived from the A ring-moiety in the β-5 building blocks. Comparison of the product yields from **I** with those from a Japanese cedar wood and its lignins suggested that the contributions of the β-5 building blocks are large to the formation of 4-methylguaiacol in pyrolysis of lignins.

1999-108
過マンガン酸カリウム酸化分解の新たな触媒を用いた改良法の開発
辻 幸子[*1]、諸星紀幸[*1]、大森茂俊[*2]
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A potassium permanganate oxidation method modified with new catalysis
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Abstract: Potassium permanganate oxidation of lignin is a very important method to be able to obtain information about lignin chemical structures, and the higher the yield of degradation products is, the more useful the method will become. Then we tried to modify the method by addition of catalysis, cetyltrimethylammonium bromide, in order to increase the yield of degradation products.

In conclusion, we got the result that the yield of degradation products of the modified method increased 10%-30% in comparison with control method.

1999-109
TIZ 分解法におけるαエーテル構造の反応性
片平　類、中坪文明
京都大学大学院農学研究科
The chemical reactivity of α ether structure in lignin in the TIZ degradation method
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Graduate school of Agriculture, Kyoto University

Abstract: Many degradation methods for β-*O*-4 structure reported so far are usually conducted under acidic or alkaline conditions, resulting in that unexpected secondary condensation reactions are caused. Therefore we have previously developed the quite novel degradation method of the β-*O*-4 structure in lignins without any secondary side reactions named TIZ method. But the stability of *α* ether structure in the degradation reactions by TIZ method has not been recognized. In this study, weshowedby β-*O*-4 lignin model experiments that α ether structures were not cleaved by TIZ method.

1999-110
過ヨウ素酸酸化によるリグニン・多糖エーテル結合の定性的及び定量的検討
藤本文[*1]、飯塚堯介[*1]、Thi Bach Tuyet Lam[*2]、飯山賢治[*3]
[*1] 東京大学大学院農学生命科学研究科, [*2]La Trobe 大学生化学科、[*3] 東京大学アジア生物資源環境研究センター
Qualitative and quantitative investigation of ether linkage between lignin and polysaccharide in plant cell walls by periodate oxidation
Aya Fujimoto[*1], Gyosuke Meshitsuka[*1], Thi Bach Tuyet Lam[*2], Kenji Iiyama[*3]
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Abstract: It is exciting to make clear the structural feature of covalent associations between lignin and wall polysaccharides, so called LCC, because of their important roles for plant physiology and effective utilization of biomass. We are focusing to elucidate linkage positions of direct ether linkages between phenylpropane unit of lignin and glycosidic residue, which would be most important linkages for periodate oxidation followed by ozonolysis to remove sugar residues and phenylpropane units free from the associations, respectively. ln this paper, we applied these procedures to cell walls of yezo spruce (*Picea jezoensis* Carr.) and investigated the optimum conditions for periodate oxidation, reduction of the residue of periodate oxidation, mild acid hydrolysis and so on. Tetra-*O*-acetyl-erithritol was detected and quantified as a major product by an alditol acetate analysis of residue of the periodate oxidation followed by reduction and mild acid hydrolysis, together with tetra-*O*-acetyl-threitol. The result suggests that the presence of linkages between lignin and the C6-position of glucosyl residue, probably cellulose, and between lignin and the C6-position of galactosyl residue. We have applied the procedures to cell walls of beech (*Fagus crenata* Blume).

1999-111
脱リグニンに伴うβ-*O*-4 型構造のエリスロ・スレオ比の変化について
杉本倫子、秋山拓也、松本雄二、飯塚堯介
東京大学大学院農学生命科学研究科
Change in E/T ratio ofβ-*O*-4 structure during delignification reaction
Tomoko Sugimoto, Takuya Akiyama, Yuji Matsumoto, Gyosuke Meshitsuka
Graduate School of Agricultura1 and Life Sciences, the University of Tokyo

Abstract: By the ozonation method, erythro and threo (E/T) ratio of arylglycerol-β-aryl ether (β-*O*-4)

structure can be obtained as a ratio between two ozonation products, erythronic and threonic acids. It was confirmed that the ozonation method can be successfully applied to a lignin remaining in partially delignified samples if degraded lignin is well washed out from the sample. This method was applied to an analysis of the change in E/T ratio in the residual lignin after wood meal was stepwisely delignified. When delignified by alkali cooking, not only the total yield of erythronic acid and threonic acid per lignin but also the E/T ratio decreased significantly with the progress of delignification. In contrast to this, when delignified by $NaClO_2$ treatment, no significant change was observed in E/T ratio. It is likely that a part of lignin with higher content of β-*O*-4 structure was rich in erythro type and was preferentially removed by alkali cooking, and , the part of lignin with low content of β-*O*-4 structure was relatively poor in erythro type and resistant to alkali cooking. These results coincide well not only with the generally accepted delignification mechanism during alkaline pulping but also with our previous hypothetical proposal that the E/T ratio of secondary wall lignin is higher than that of compound middle lamella lignin. On the other hand, when delignified by $NaClO_2$, the delignification seems to proceed almost homogeneously regardless of the content of β-*O*-4 structure and its E/T ratio. It is well understood from its reaction mechanism to oxidize lignin.

1999-112
バングラデシュ産アカシア・カテチュ心材抽出物の化学組成
アブル・カラム・アザド、荻山紘一
山形大学農学部
The chemical constituents of Bengal catechu (*Acacia catechu*)-heartwood extractives
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Faculty of Agriculture, Yamagata University
Keywords: (+)-catechin, NMR spectrometry, PTLC. GC-MS
Abstract: Acacia catechu に属するベンガル・カテチュの水抽出物は，ベテルの葉（地方名パン）のスパイスとしてチューインガムに昔から用いられている．この樹木の赤色心材の主化学成分は，バングラデシュではカテチュと呼ばれている．心材のメタノール抽出物（収量 8.64%）の TLC 分析は，この部分に 9 個のフェノール性化合物が存在することを示した．この抽出物の主ポリフェノール化合物は，（＋）-カテキンで，メタノール抽出物の約 3.33%を占めていた．その母液から新規な化合物が単離された．それは（＋）-カテキンと同じ A 環と B 環を持ち，七員ヘテロ環状の C 環を有していた．その収量は，メタノール抽出物の約 0.053%であった。

1999-113
ゴボウ（*Arctium lappa*）におけるセコイソラリシレジノール生成の立体化学的選択性について
鈴木史朗、梅澤俊明、島田幹夫
京都大学木質科学研究所
Stereochemical selectivity of secoisolariciresinol formation in *Arctium lappa* L.
Shiro Suzuki, Toshiaki Umezawa, Mikio Shimada
Wood Research Institute, Kyoto University
Abstract: The difference in stereochemistry of secoisolariciresinol formation between petioles and ripening seeds of *Arctium lappa* L. was further investigated using the cell-free extracts. Both cell- free extracts from ripening seeds and petioles catalyzed the formation of (-)-secoisolariciresinol from (±)pinoresinols and (±)lariciresinols, but with different enantiomeric compositions of the product. However, we previously reported the enantioselectiveformation of (+)secoisolariciresinol from coniferyl alcohol using cell-free extracts from the petioles. These results indicate that stereochemistry of lignan biosynthesis in *A. lappa* is very complicated and diverse.

1999-特別講演、I.
植物の外部環境検知能力と形づくりについて
野方文雄
岐阜大学工学部
Cell-based sensing system for external stimuli and an adaptive modeling process in plant
Fumio Nogata
Department of Mechanical and Systems Engineering, Gifu University
Abstract: Examining some biological load carriers such as plant and tree stems, animal bones and other

biological hard tissues, we see that their geometry changes under loading to match mainly stress- or strain-dependent requirements. For example, the interior structure of a bone exhibits all optimized shape with respect to the principal stress directions and the shear stress magnitude in the body. This indicates that the bone is managed by a self-optimizing system with sensing mechanisms (e.g., piezoelectric and/or streaming potential effect of bone) that detect external mechanical stimuli to control the modeling/remodeling of the skeletal system. Thus, it can be inferred that the shape and ingenious construction of biological hard tissues are the result of a continuous process of intelligent optimization. The goals of this work are to gain an understanding of the principles of design and processes found in biological tissues and to apply these findings toward developing new, intelligent, superior material concepts by using and/or modifying those models which are found in living organisms. We begin by presenting bamboo as a typical example of the ingenious construction, depending on mechanical stresses/strains conditions, and a cell based sensing system for external stimuli as well as an adaptive modeling process in plant.

1999-特別講演、II.

リグニン生分解研究から派生したシュウ酸合成酵素研究への新局面。—木質資源の育成と保護に関わる菌類の役割—

島田幹夫
京都大学木質科学研究所

A new aspect of oxalic acid producing enzyme research derived from lignin biodegradation research, —Roles of fungi in production and preservation of woods

Mikio Shimada
Wood Research Institute, Kyoto University

Abstract: Retrospective viewpoints of lignin biodegradation research are described focusing on development of the first biomimetic example of heme enzyme (LiP and MnP) model catalysts for the one electron oxidation of lignin and bleaching of unbleached kraft pulps. A new aspect of oxalic acid involved in ligninolytic systems in white-rot fungi is discussed in relation to a possible role of the glyoxylate cycle which may commonly occur in a wide variety of saprophytic, symbiotic, and edible mushrooms.

1999-201

耐塩性白色腐朽菌に関する研究（I）高塩濃度条件下で生育する菌株の探索

李 シン、近藤隆一郎、坂井克己
九州大学大学院生物資源環境科学研究科

Study on hypersaline-tolerant white-rot-fungi. (I). Screening of lignin-degrading fungi at hypersaline

Li Xin, Ryuichiro Kondo, Kokki Sakai
Faculty of Agriculture, Kyushu University

Abstract: In order to characterize marine fungi, which have high lignin-degrading ability at saline conditions, several marine fungi were screened from 28 fungus strains isolated from mushrooms and driftwood samples from the mangrove stands in Okinawa, Japan. The decolorization ability, delignification activity of wood meals and biobleaching property were evaluated and then a strain MG-60, was selected as a prosperous marine fungus that had tolerance to hypersaline.

1999-202

白色腐朽菌 *Ceriporiopsis subvermispora* の生産する新規ジカルボン酸

榎 牧子、本田与一、渡辺隆司、桑原正章
京都大学木質科学研究所

A novel dicarboxylic acid produced by white-rot fungus *Ceriporiopsis subvermispora*

Makiko Enoki, Yoichi Honda, Takashi Watanabe, Masaaki Kuwahara
Wood Research Institute, Kyoto University

Abstract: Novel fluorescent dicarboxylic acids, 1-heptadecene-2,3-dicarboxylic, 1,7-nonadecadiene 2,3-dicarboxylic and 1-nonadecene-2,3-dicarboxylic acids were isolated from wood meal cultures of white-rot fungus *Ceriporiopsis subvermispora*. These three compounds are itaconic acid derivatives having different aliphatic chain. The amount of these amphiphilic dicarboxylic acids increased with incubation time, suggesting that production of these dicarboxylic acids is related to lignin biodegradation.

1999-203

マンガンペルオキシダーゼによる非フエノール性リグニンモデル化合物の分解

鬼束愛子、近藤隆一郎、坂井克己
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Degradation of non-phenolic lignin model compounds by manganese peroxidase

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Abstract: We previously reported that isolated manganese peroxidase (MnP) from white rot fungus *Phanerochaete sordida* YK-624 cleaved β-ether bond of 3-hydoroxy-2-(4-methyl- umbelliferone)-1-phenylpropanone. The system required MnP, malonate, Tween 20 and MnSO4 but not hydrogen peroxide. In this study, we tried to degrade nonphenolic lignin model compounds having α-carbonyl or α-hydroxyl group by MnP from *P. sordida* YK-624. Model compounds having α-carbonyl group were degraded by MnP system (MnP, malonate, Tween 20. and MnSO4), however. model compounds having α-hydroxyl group were not degraded at all. The reaction mechanism will be discussed.

1999-204

白色腐朽菌 *Pleurotus ostreatus* により生産される MnP アイソザイムの生産調節について

上辻久敏、河 考哲、本田与一、渡辺隆司、桑原正章
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The effect of culture condition on the production of manganese peroxidase by white-rot fungi *Pleurotus ostreatus*

Hisatoshi Kamitsuji, Ha Hyo-cheol, Yoichi Honda, Takashi Watanabe, Masaaki Kuwahara
Wood Research Institute, Kyoto University

Abstract: Manganese peroxidase (MnP) was secreted by *Pleurotus ostreatus* in liquid stationary culture. Two different MnP isozymes were produced in glucose/yeast-extract medium (GY) and peptone/glucose/yeast-extract medium (PGY). The isoelectric points of MnP produced in GY medium (MnP-GY) and PGY medium (MnP-PGY) were found to be 3.70 and 3.95, respectively. The molecular masses of both isozymes were 42 kDa. N-terminal amino acid sequences of MnP-PGY was found to be identical to that of MnP 3. It was also similar to that of MnP which was produced in the sawdust culture.

1999-205

白色腐朽菌ヒラタケにおける組換えマンガンペルオキシダーゼ発現系の開発

入江俊一、本田与一、渡辺隆司、桑原正章
京都大学木質科学研究所

Homologous expression of recombinant manganese peroxidase gene in *Pleurotus ostreatus*

Toshikazu Irie, Yoichi Honda, Takashi Watanabe, Masaaki Kuwahara
Wood Research Institute, Kyoto University

Abstract: The genomic and cDNA fragments encoding *Pleurotus ostreatus.* MnP3 were cloned and analyzed. From sequencing analysis, it was demonstrated that *P. ostreaus* MnP3 has a property specific for both of manganese peroxidase and lignin peroxidase from *Phanerochaete chrysosporium*. The coding sequence was fused with promoter and terminator sequence of *P. ostreatus sdi1* encoding succinate dehydrogenase iron-sulfur protein subunit. The recombinant constructs were introduced into wild-type *P. ostreatus* strain *via* DNA-mediated transformation. Transformants which express higher MnP activity than wild type were isolated. One of the recombinants obtained by mating between two monokaryotic transformants, TMG9-C1 has shown several times higher MnP activity than the wild-type control in the early stage of liquid culture of the mycelium. Predominant transcription of the recombinant *mnp3* at the 6th day was demonstrated by a competitive RT-PCR experiment.

1999-206

シロアリ腸内から単離した放線菌の産生するペルオキシダーゼについて

原園幸一[*1]、渡辺吉雄[*2]、深津武馬[*1]、倉根隆一郎[*1]
[*1] 工業技術院生命工学工業技術研究所、[*2] メルシヤン中央研究所

Peroxidase produced by *Streptomyces eurythermus* isolated from guts of lower termites, *Coptotermes formosanus*

Koichi Harazono[*1], Yoshio Watanabe[*2], Takema Fukatsu[*1], Ryuichiro Kurane[*1]
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Industrial Science and Technology, [*2]Central Research Laboratory, Mercian Corp.

Abstract: The production of peroxidase by actinomycete, *Streptomyces eurythermus* CA2 isolated from guts of lower termites, *Coptotermes formosanus* was studied in shaken liquid culture.

The addition of 5-aminolevulinic acid increased peroxidase activity in culture of *S. eurythermus* CA2. Peroxidase activity in culture of *S. eurythermus* CA2 was dependent on H2O2 and was inhibited with potassium cyanide and ethylene glycol bis(-aminoethyl ether) N,N,N',N'-tetraacetic acid (EGTA). Four peroxidase isozymes from concentrated culture filtrate were detected by nondenaturing polyacrylamide gel electrophoresis (PAGE) and activity staining with L-3,4-dihydroxyphenylalanine as the substrate. The molecular mass of main peroxidase isozyme P2 was about 53 kDa.

1999-207

白色腐朽菌の液体培養系による飛灰中ダイオキシン類の分解

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Degradation of dioxins in fly ash treated in the liquid culture of white rot fungi
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Faculty of Agriculture, Kyusyu University

Abstract: Seventy two strains of fungi were screened for the growth in the liquid medium mixed with fly ash. White rot fungus MZ-340 was selected, because it grew well in the medium mixed with fly ash, and degraded 2,7-dichlorodibenzo-*p*-dioxin extensively. In this study, we demonstrated the degradation of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/DFs) in fly ash by the liquid culture of the fungus. PCDDs/DFs content, 52.0 ng-TEQ/g, in the fry ash were reduced to l 8.6 ng-TEQ/g by treatment with the fungus MZ-340 for 2 weeks.

1999-208

ラッカーゼおよびマンガンペルオキシダーゼによる内分泌撹乱物質の除去

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Removal of endocrine disrupters by laccase and manganese peroxidase
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Abstract: Endocrine disrupters, such as bisphenol A (BPA) and nonylphenol (NP), may modify natural endocrine function and so affect human health and wildlife. In this study, therefore, we tried to remove the estrogenic activity of BPA wd NP with partially purified laccase and manganese peroxidase (MnP). BPA and NP were removed by both enzyme treatments in 60 min, which was mainly due to polymerization. We also measured the estrogenic activity of-BPA or NP before and after enzyme treatments by using yeast two-hybrid system. More than 95% of estrogenic activity of BPA and NP disappeared after 12h-treatment with both enzymes. These findings indicate that the treatment of BFA and NP with laccae and MnP is effective in removal and disappearance of estrogenic activity of them.

1999-209

リグニン分解酵素系によるパルプ繊維の改質　―MnP 処理が DIP パルプ繊維に及ばす影響―

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Application of ligninolytic enzymes to modification of pulp fibers. -Effects of MnP treatment on DIP
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Abstract: The application of MnP treatment to DIP was examined. The ISO brightness of the DIP decreased slightly by MnP treatment, however, it was recovered with the combination of H2O2 bleaching. The residual fluorescence intensity in DIP was decreased by MnP treatment. Physical properties of DIP was improved by Map treatment, and also Map treatment enhanced the effect of PAM addition on physical strength of the pulp.

1999-210

溶媒循環プロセスによる HBS パルプ化（1）―針葉樹材の脱リグニン

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北海道大学大学院農学研究科
HBS pulping with solvent-recycling process. (I). -Delignification of softwood.
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Abstract: In order to develop a new pulping process with non-pollution and saving energy, softwood was subjected to delignification with high boiling-pint solvents (HBS) with and without acetic add. Todomatsu, ezomatsu, karamatsu and sugi were easily delignified under conditions with 60-80% HBS such as butanediol-1,4 at 220ºC for 1-3 h with and without acetic acid. However, acetic add promoted the delignification reaction. Pulp was washed with the same solvent or acetone, and then water. The water washing was poured into a mixture of the reaction liquor and solvent washing to precipitate water insolubles such as lignin and sugar modified products. A mixture of solvent and sugars recovered by evaporation of the water from water solubles could be reused more than 5 times as a pulping solvent for the new pulping procedure without hitch.

1999-211
硝酸と亜硝酸塩を添加した有機溶媒水媒体における広葉樹リグニンの分解挙動
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筑波大学農林工学系
Behavior of hardwood lignin decomposition in organic solvent-water media with nitrite and nitric acid
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Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: Ethanol-water pulping has been proposed as one of organosolve pulping methods. Acid catalysts were investigated for improving the pulping conditions, but nitric acid is not studied yet. Nitric acid pulping is conducted at much lower temperatures than the ethanol-water pulping. The effects of nitrite and nitric acid on the pulping using ethanol-water media are not clear. It has been shown that at the dosage of 40% nitric acid and 90ºC, the lignin decomposition was facilitated when a very small amount of catalytic nitrite was added. In addition, the pH of the media was increased by the consumption of nitric acid. In this study, behavior of lignin decomposition in such media is further discussed using an isolated lignin and wood chips.

1999-212
塩素漂白過程で生成するクロロホルムの可能生成量について
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東京大学大学院農学生命科学研究科
Formation potential of chloroform during chlorine bleaching of kraft pulp
Keiichi Koda, Hiroyuki Shintani, Yuji Matsumoto, Gyosuke Meshitsuka
Graduate School of Agricultural and Life Sciences, The University of Tokyo

Abstract: Chlomform produced during chlorine bleaching of kraft pulp was quantitatively analyzed by GC-MS (SIM mode). The amount of chloroform that can potentially be formed was also estimated. Chlorination and alkali treatment of pulp and/or effluent was performed in a gas tight reaction vessel in order to determine chloroform as accurately as possible. The result suggested that by subjecting both chlorinated pulp and chlorination effluent to alkali treatment, chloroform precursors were quantitatively estimated. Even though hypochlorite addition is the major source of chloroform formation, chloroform formation during both C-and E-stages should properly be evaluated.

1999-213
マルチング中の剪定枝チップ細胞壁成分の変化
小野　芳[*1]、市川朋子[*1]、渡辺達三[*2]、飯山賢治[*3]
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Compositional changes of wood chips during mulching
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Abstract: Huge quantities of pruned branches are produced from planted trees at urban area. Recently, they are utilized in the shape of wood chips as compost and mulch. In this paper, sequential changes in wood chip mulch were examined by using *sugi* (*Cryptomeria japonica*) and *keyaki* (*Zelcova serrata*). Changes in chemical composition were also investigated for wood chips buried at the bottom and the surface of mulch system. It was shown that *Z. serrata*, an Angiosperm wood, was modified biologically faster than *C. japonica*, a Gymnosperm wood, and compositional changes in mulch buried in the bottom was more significant than that at surface. The relative content of lignin increased significantly in *Z. serrata* mulch, and condensation of lignin made progress during mulching.

1999-214
リグニン系土壌改良剤による植物の AL 生育障害の改善
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東京大学大学院農学生命科学研究科
Improvement of growth inhibition of plant by AL using soil conditioning agent from lignin
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Graduate School of Agriculture and Life Sciences, The Umiversity of Tokyo

Abstract: Aluminum ion (AL) is one of the main reasons of toxicity to plant growth in acid soil. AL is eluted from soil matrix below pH 4.5 and inhibits elongation of plant root. We modified krait lignin by alkaline-oxygen treatment and obtained humin-like materials rich in acidic groups, especially carboxylic acid group. Modified kraft lignins were expected to form complex with AL, which has been confirmed by pH titration. In this study, the effect of pH and the formation of AL-lignin complex on grow of radish root were examined. It was found that toxicity of AL dissolved in the culture solution was effectively removed by the presence of enough amount of a modified lignin.

1999-215
両親媒性リグニン誘導体と蛋白質の相互作用
西田光邦、浦木康光、佐野嘉拓
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Interaction of amphiphilic lignin derivative with protein
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Graduate School of Agriculture, Hokkaido University

Abstract: Acetic acid ligmin (AL) prepared by the atmospheric acetic acid pulping of birch was reacted with polyethylene glycol diglycidyl ether (PE) under alkaline conditions to yield an amphiphilic AL derivative (PE-AL). PE-AL was suggested to have a similar structure to the rigid Binstein's sphere in aqueous solution, and to shrink as increasing in the concentration probably due to the hydrophobic interaction of AL domains by viscometric study. PE-AL was found to form the complex with bovine serum albumin as model protein for about one week at 4°C by the measurements of size-exclusion chromatography and circular dichroism. Furthermore, the decrease in lipase activity in aqueous 20% ethanol was repressed by PE-AL. Thus, PE-AL seems to contribute to preserve the activity of enzyme.

1999-216
リグニンベースポリカプロラクトン誘導体の TG・FTIR
畠山兵衛[*1]、吉田孝範[*1]、伊豆田良信[*1]、廣瀬重雄[*2]、畠山立子[*3]
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TG-FTIR of lignin-based polycaprolactone derivatives
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[*1]Fukui Institute of Technology, [*2]National Institute of Materials and Chemical Research, [*3]0tsuma Women's University

Abstract: Lignin-based polycaprolactone derivatives (LigPCL) were prepared from kraft lignin (KL) and an organosolv lignin (Alcel lignin, AL). The gases evolved by thermaldegradation of LigPCL were analyzed by simultaneous thermogravimetry (TG) and Fourier-transformed infrared spectrometry (TG-FTIR). The amounts of thermal degradation products having characteristic functional groups changed according to the length of PCL chains in the LigPCLs.

1999-P01
広葉樹シリンギルリグニンの生成機構

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名古屋大学大学院生命農学研究科

Biosynthesis of syringyl lignin in angiosperm

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Faculty of Agriculture, Nagoya University

Abstract: 4-Coumarate:CoA ligase (4CL) activity for sinapic acid has not been detected in many dicotyledonous plants. In order to investigate the existence of the pathway (sinapic acid to sinapoyl-CoA), we perform the tracer experiment. Sinapic acid, both two methoxyl groups were labled by deuteriums, was synthesized and fed to various angiospermous wood. If the pathway (sinapic acid to sinapoyl-CoA) exists, two labled methoxyl groups should be intrduced to lignin.

1999-P02

広葉樹分化中木部細胞における O-メチルトランスフエラーゼの局在

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Localization of OMT in differentiating xylem cells of hard wood

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Abstract: Considerable works has revealed the presence of enzymes involved in lignin biosynthesis, and the biosynthetic pathway of lignin is, now, generally accepted. However, the localization of each enzyme in cell is still open to discussion. *O*-Methyl transferase (OMT) catalyzes reactions from caffeic acid to ferulic acid or from 5-hydroxyferulic acid to sinapic acid. We produced rabbit anti-OMT antibody by using a fusion protein of a part of OMT and histidine as an antigen. Immunocytochemistry revealed localization of OMT at differentiating xylem cells of *populus* and *eucalyptus*. Labelings of OMT was not observed on any organelles but on cytosol.

1999-P03

シナピルアルコールの酵素的脱水素重合に対するコニフェリルアルコール混合の影響

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Effect of the mixing of coniferyl alcohol on the enzymatic dehydrogenative polymerization of sinapyl alcohol

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Abstract: Sinapyl alcohol reacts very slowly by horseradish peroxidase (HRP) comparing with other monolignols, but it reacts so fast by addition of guaiacyl or *p*-hydroxyphenyl compound. Some phenolic materials were used to investigate the influence of their functional groups on the HRP reaction. Further, the posibility of the radical transportation was investigated by two-layer system in which sinapyl alcohol was separated from HRP by ultra filter. From the results, we proved that some phenolic materials play a roll as a radical mediator.

1999-P04

分子軌道法による種々の溶媒中でのリグニン前駆体のコンフオメーション解析

重松幹二、小林孝行、棚橋光彦
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Molecular orbital analysis on the conformations of monolignols dissolved in various solvents

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Faculty of Agriculture, Gifu University

Abstract: Solvent effect on the optimum conformations of monolignols was computer-simulated by MOPAC97 program including PM3 and COSMO methods. In the cases of guaiacol and coniferyl alcohol, the Boltzman's probability of hydrogen bond between phenolic hydroxyl and methoxyl groups was decreased by increase of the dielectric constant of solvent, for example, 96% in gas phase, 86% in benzene, 48% in pyridine and 36% in water. In the cases of 2,6-dimethoxyphenol and sinapyl alcohol, the 60% of phenol hydrogen oriented to either of two methoxyl oxygens in gas phase, but less than 30% in water.

1999-P05

リグニンの NMR におけるシフト試薬の効果

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The effect of shift reagents on NMR spectra of lignin

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Abstract: The shift reagents have been applied for the separation of overlapped peaks in NMR spectra. ln this paper, the effect of Eu-FOD and Pr-FOD, which are common shift reagents, on NMR spectra of lignin was investigated. Signals in ^{1}H-NMR spectra of acetylated MWL (milled wood lignin) were broadened by the addition of those shift reagents, and the resolution of spectra became even worse. The main reason for this result must be the difficult complex formation caused by the bulkiness of lignin molecule. Further modifications of conditions (ex. solvent, temperature, kind of derivatization) are needed for the effective application of shift reagents on NMR spectrometry of lignin.

1999-P06

セプターパヤ細胞壁の成分とタンニンの特徴

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Characteristics of cell wall components and tannins from the wood of *Pseudosindora palustris*

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Abstract: *Pseudosindora palustris* wood contained 18.9% of polyphenols and 23.6% of acid insoluble lignin. From acetone-water (7:3) extracts of he wood fisetinidol and fisetinidol-(4α→8)- catechin were isolated after separation by column chromatography. ^{13}C-NMR spectra indicated that polymers from the acetone-water extracts were prpanthocyanldin polymers which mainly consisted of profisetinidin. On-line methylation pyrolysis-gas chromatography gave 3, 4-dimethoxytoluene from die B ring, 1, 3-dimethoxybenzene from the A ring, and a pyrolysis product which was assumed to be 1-(2-methoxyethyl)-2, 4, 6-trimethoxybenzene. It has been made clear that the proantho- cyanidin polymers consist of profisetinidin units including a small number of procyanidin units.

1999-P07

チヤボヒバ(*Chamaecyparis obtusa* cv. Breviramea)から単離された新規リグナンについて

高久尚裕、奥西智哉、三亀啓吾、鈴木史朗、梅澤俊明、島田幹夫
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A new lignan from *Chamaecyparis obtusa* cv. Breviramea

Naohiro Takaku, Tomoya Okunishi, Keigo Mikame, Shiro Suzuki, Toshiaki Umezawa, Mikio Shimada
Wood Research Institute, Kyoto University

Abstract: A new lignan, which is an isomer of actifolin named isoactifolin, and three known lignans, dihydrosesamin, piperitol, and sesamin, were isolated from the methanol extracts of leaves of *Chamaecyparis obtusa* cv. Breviramea.

1999-P08

ニオイヒバリグナンの検索とそれらリグナン類の生合成について

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岐阜大学農学部

Isolation and identification of *Thuja occidentalis* lignans and their biosyntheses

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Abstract: Five lignans, (8*R*, 8'*R*)-(-)-yatein, dihydroxythujaplicatin methyl ether, thujastandin, lariciresino, pinoresinol were isolated from *Thuja occidentalis* xylem, besides the previously identified seven lignans. Chiral HPLC analysis of yatein indicated that the compound was optically pure. The presence of secoisolariciresinol was also identified by GC-MS analysis of the extract of *T. occidentalis* xylem. Feeding experiments of [9, 9-^{2}H2, OC^{2}H3]coniferyl alcohol and [7, 7-^{2}H2, 3'-

OC^{2}H3] secoisolariciresinol into *T. occidentalis* young shoots resulted that two molecules of coniferyl alcohol were incorporated into pinoresinol and lariciresinol, and secoisolariciresinol was incorporated into lariciresinol.

1999-P09

数種の培養細胞を用いたリグナン、ポドフィロトキシンのバイオトランスフォーメーションによるリナン配糖体の調製の試み

内藤隆行、伊藤和貴、橘　燦郎
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Trial for preparation of podophyllotoxin glucoside by biotransformation of podophyllotoxin by use of some plant cell cultures

Takayuki Naito, Kazutaka Ito, Sanro Tachibana
Faculty of Agriculture, Ehime University

Abstract: Production of podophyllotoxin glucoside by biotransformation of podophyllotoxin by use of cell suspension cultures of *Gardenia jasminoides*, *Nicotiana tabacum* and *Datura innoxia* was tried. From the results of HPLC analysis of each reaction product, we found that podophyllotoxin glucoside was produced by the cultures of *D. innoxia* in the maximum yield of 4.6%. However, the glucoside could not be produced by the cultures of *G. jasminoides* and *N. tabacum*.

1999-P10

Mn(II)酸化能を有する微生物に関する研究

西中亜紀子、堤　祐司、西田友昭
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Studies on Mn(II)-oxidizing microorganisms

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Abstract: Screening of microorganisms which can oxidize Mn(II) to Mn(III) was attempted. One of such microorganism from literatures, *Leptothrix discophora* SS-1(SS-1), was examined its potential of Mn(III) formation from Mn(II). The prepared crude enzyme from SS-1 could oxidize Mn(II) to MnOx and effectively convert Mn(II) to Mn(III) in the presence of pyrophosphate as a chelator of Mn(III). Also, 336 of positive bacterial colonies were isolated from the samples collected from Taguchi mine, Japan, by their ability of MnOx formation from Mn(II) on the plate. Twenty-six colonies were further selected from 336 and their ability of Mn(III) formation is in progress.

1999-P11

白色腐朽菌が産生するマンガンペルオキシダーゼ活性化物質について

扇　剛士、鬼束愛子、近藤隆一郎、坂井克己
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Production of extracellular manganese peroxidase activity-stimulating substances by white rot fungi

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Faculty of Agriculture, Kyusyu University

Abstract: Manganese peroxidase (MnP) is an extracellular heme protein produced by wood-rotting and litter-degrading basidiomycetes especially during secondary metabolism. MnP catalyzes the H2O2-dependent oxidation of phenolic lignin structures. We had interest in producing of extracellular MnP activity-stimulating substances by white rot fungi. *Phanerochaete sordida* YK-624 and *P. chrysosporium* were cultivated in the liquid medium, and extracellular low molecular-weight substances were prepared. Addition of extracellular substances, which is equivalent amounts of Mn to MnSO4, to the MnP reaction mixture increased the MnP activity comparing with MnP-MnSO4 system. Addition of Kirk medium instead of MnSO4 to the reaction mixture did not increase the MnP activity. These results suggest that white rot fungi night produce extracellular MnP activity- stimulating substances.

1999-P12　（発表中止）

1999-P13

白色腐朽菌 MZ-340 株の 18SrDNA による系統学的分類

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Taxonomy of the white rot fungus MZ-340 using 18SrDNA
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Abstract: Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have been a public concern for several decades because of their strong toxicity. We have suggested that one white rot fungus, tentatively named strain MZ-340, collected from natural forest in Japan, can degrade PCDDs and PCDFs. To identify the classification of the strain MZ-340, nucleotide sequences of the small subunit ribosomal RNA gene were examined. The strain MZ-340 was closely related to *Phanerochaete chrysosporium* or *Phlebia radiata* when searched with “DDBJ BRAST search”. Subsequently phylogenetic relationship of strain MZ-340 was investigated by "Phylip package” using our sequences and data on “GenBank”. Based on our current data, strain MZ-340 could be classified as family of *Corticiaceae* including genus of *Phanerochaete* and *Phlebia.*

1999-P14
白色腐朽菌によるダイオキシン類の *in vitro* 分解 (III) ～MZ-340 株産生酵素の基質特異性について～
森智夫、近藤隆一郎、坂井克己
九州大学大学院生物資源環境科学研究科
In vitro degradation of dioxins by white rot fungi (III), ～Substrate specificity of extracellular enzyme from the fungus MZ-340～
Toshio Mori, Ryuichro Kondo, Kokki Sakai
Faculty of Agriculture, Kyushu University

Absreact: The white rot fungus strain MZ-340 was screened as the strain having dioxins- degrading ability. We have previously reported that culture filtrate from the strain MZ-340 can degrade 2,7-dichlorodibenzo-*p*-dioxin and 2,8-dichrlorodibenzofuran. The purpose of present study was to examine whether biarylic compounds such as dioxins or dioxin like compounds can be degraded by the culture filtrate from the strain MZ-340. 2,7 dichlorodibenzo-*p*-dioxin, 2,8-dichloro- dibenzofuran and 4,4’-dichlorobiphenyl were reacted with the filtrate, although non-chlorinated compounds, dibenzo-*p*-dioxin, dibenzofuran and biphenyl were not. Probably, chlorine-substitution will be important in this enzymatic reaction.

1999-P15
担子菌におけるケミカルストレス応答タンパク質の検索
森下大史、一瀬博文、栗原宏征、割石博之、田中浩雄
九州大学農学部
Search for the new proteins from the basidiomycetes
Hiroshi Morishita, Hirofumi Ichinose, Hiroyuki Kurihara, Hiroyuki Wariishi, Hiroo Tanaka
Faculty of Agriculture, Kyushu University

Abstract: To investigate the mechanism of substrate recognition and metabolic response, 2-dimensional protein electrophoresis and differential display techniques were utilized. The cell free extracts prepared from fungal hyphae in the presence of the chemical stress were compared with those from non-stressed cell. Dioxins, biphenyls, and dibenzothiophenes were utilized as a chemical stress, since their metabolic pathways were at least partially elucidated. The addition of these compounds resulted in the appearance of new proteins and the expression of specific genes.

1999-P16
木材腐朽菌によるケナフパルプの漂白
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高知大学農学部
Biobleaching of kenaf bast pulp by wood rot fungi
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Abstract: Biobleadhing of kenaf bast pulp was tried using some wood-rot fungi screened and isolated from the field and typical ones; *Pleurotus ostreatus* and *Phanerochaete chrysosporium*.
Each fungus precultured in Kirk medium was inoculated upon kenaf bast pulp and incubated statically at 29ºC. The mest effective fungus was OM5-1 screened in our laboratory. It has an ability to increase pulp brightness 2 tines larger and to decrease kappa number 1.5 tines larger than *P. chrysosporium*. It also showed higher initial

Mn peroxidase activity than *P. chrysosporium*.

1999-P17

溶媒再循環プロセスによる HBS パルプ化（2）—広葉樹材および草本類の脱リグニン—

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HBS pulping with solvent-reycling process (2), —Delignification of hardwood and annual plants—

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Abstract: In order to develop a new pulping process with non-pollution and saving energy, hardwood (birch and commercial *E. globulus*) and annual plants (kenaf, palm oil wastes, rice and wheat straws, and bagasse) were subjected to delignification by HBS pulping prpocess with high boiling-point solvents (HBS) with and without acetic add. They were significantly delignified at 200ºC for 3 h without acetic acid and for 2 h with 5-10% AcOH of the solvent. The RHBSs removed only lignin from pulping waste liquors were possible to reuse several times as pulping solvent.

1999-P18

常圧酢酸パルプ化 —パルプ廃液から得られる糖成分の考察

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Atmospheric acetic acid pulping, -Carbohydrate in water solubles fractionated from waste liquor

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Abstract: Atmospheric acetic acid pulping (AcOH pulping) is one of the organosolv pulping aimed at total utiliziation of biomass. Birch, todomatsu and rice and wheat straws were fractionated into pulp, lignin and water solubles by the pulping. Each water solubles were obtained in yields of 20-30% of raw material and contained monosaccharides (sugars,40-50% of water solubles) and colored substances. The sugars were easily purified with carbon-celite, following by conversion to alditols by catalytic hydrogenolysis with Raney Nickel. The alditols purified by ion-exchange resin were analyzed.

1999-P19

自己会合性ヒドロキシプロピルリグノセルロース誘導体の溶液挙動

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Solution property of self-assembled hydroxypropylated lignocellulose derivative

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Abstract: Solution behavior of hydroxypropylated (HP) lignocellulose that was prepared from acetic acid pulp was investigated by the small angle X-ray scattering (SAXS) and the measurement of lower critical solution temperature (LCST) to clarify the self-assembly. Kratky plot of SAXS indicated that HP-lignocellulose was a rod-like polymer both in water and tetrahydrofuran as well as commercially HP-cellulose (HPC). The cross-sectional radium of gyration was found to increase with the increase in residual lignin content by Guinier plot. LCST of HP-lignocellulose was approximately 36ºC, while HPC had LCST above 39ºC. These results suggest that the residual lignin in the self-assembled HP-lignocellulose remarkably affected polymer structure and phase separation in the solution.

第45回（2000.10.26-27）愛媛大学農学部

2000-101

広葉樹シリンギルリグニンの生成機構

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The biosynthetic mechanism of syringyl lignin in angioperm

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Abstract: There is a great interest in the question whether sinapic acid is the true precursor of syringyl lignin or not, because the activity of 4-coumarate:CoA ligase (4CL) for sinapic acid was not detected in many angiosperms. We synthesized labeled sinapic acid-[2OMe-*d6*,β-*d*] and [2OMe-*d6*,β-^{13}C], and administered into angiosperms *(Nerium indicum* Mill. and *Robinia pseudoacacia* L.). The newly formed xylem of administered woods was analyzed by DFRC method. Labeled sinapic acid was incorporated into the syringyl lignin accompanied by all labels. Our results suggested the existence of the pathway from sinapic acid to sinapy1 alcohol via sinapoyl CoA.

2000-102

コニフェリルアルコールの脱水素重合中に生成するシリンギル核

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Syringyl units generated during the polymerization of coniferyl alcohol

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Syringyl (S) and *p*-hydroxyphenyl (H) units were detected in addition to guaiacyl (G) unit in thioacidolysis products of the DHP prepared from only coniferyl alcohol by peroxidase- H202 system. We established the appropriate condition for the formation of S and H units during the polymerization of coniferyl alcohol. We also prepared DHPs from methoxyl-*d*-labeled coniferyl alcohol to clarify the mechanism for the formation of S and H units, but we could not prove the transference of methoxyl groups.

2000-103

シリンギルリグニン生合成におけるシナップ酸と 4-Coumarate: Coenzyme A Ligase の役割

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The role of sinapic acid and 4-coumarate: coenzyme A ligase in syringyl lignin biosynthesis

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Abstract: We investigated the involvement of sinapic acid (SA) and 4-coumarate: Coenzyme A ligase (4CL) in syringyl lignin biosynthesis. Deuterated ferulic acid (FA) [3-OD3,β-D] and SA [3,5-OCD3,β-D] were administered to poplar (*Populus alba* L.) callus cultures as precursors of lignin. The thioacidolysis analyses of the administered calluses showed that the deuterated SA was not converted to guaiacyl and syringyl lignins, while SA administration clearly increased syringyl lignin content in the callus. 4CL activity against SA was not observed in the homogenized cell, crude enzyme, and microsome preparations by an enzyme assay using ^{14}C-labeled SA. The results suggest that SA is not a precursor of syringyl lignin *per se* but induces or enhances syringyl lignin biosynthesis in the callus.

2000-104

ヒャクニチソウ管状要素分化過程における細包外リグニン前駆体の存在とリグニン化への影響

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[*1] 愛媛大学理学部、[*2] 京都大学木質科学研究所、

Existance of extracellular lignin precursors and their effects on lignification during tracheary element differentiation of *Zinnia*

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Abstract: We investigated how and whence monolignols are supplied to tracheary elements (TEs) undergone programmed cell death using an experimental system of TE differentiation from isolated *Zinnia* mesophyll cells. Alternations of culture condition indicated that monolignols were supplied to TEs through medium. Analyses by HPLC and GC-MS showed that coniferyl alcohol were mainly accumulated in cultured medium. The concentration of coniferyl alcohol peaked at the beginning of secondary wall thickening, decreased during secondary wall thickening, then increased again. These results indicated that lignification of TEs progressed by supply of monolignols from not only TEs themselves but also surrounding xylem parenchyma-like cells.

2000-105

アスパラガス培養細胞の産生する *cis*-ヒノキレジノールの生合成機構について

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The biosynthesis of *cis*-hinokiresinol produced by cultured cells of *Asparagus officinalis* L.
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Abstract: The biosynthesis of a norlignan, *cis*-hinokiresinol, was studied by feeding of labelled compounds into cultured cells of *Asparagus officinalis* L. treated with fungal elicitor. The SIM-MS analysis showed that two ^{13}C atoms were incorporated into a single molecule of *cis*-hinokiresinol when [7-^{13}C1]cinnamate and [8-^{13}C1]cinnamate were administered individually to the cells, while only one ^{13}C atom originated from [9-^{13}C1]cinnamate was incorporated into the compound. The NMR analysis of *cis*-hinokiresinol produced by the cells fed with [9-^{13}C1]cinnamate revealed the incorporation of a single ^{13}C atom into the 9-position of *cis*-hinokiresinol. The cells administered with 4-[8-^{13}C1, *ring*-^{13}C6]coumarate produced *cis*-[^{13}C14]hinokiresinol. These results unequivocally indicated for the first time that *cis*-hinokiresinol was formed by the coupling of two phenylpropanoid monomer units with the loss of one carbon of the 9-position of the monomer.

2000-106

Sphingomonas paucimobilis SYK-6 株のリグニン代謝に関わる脱メチル化酵素機能の多様性と遺伝子配置

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An enzymatic diversity involved in the O demethylation of lignin metabolism and the gene arrangement in *Sphingomonas paucimobilis* SYK-6
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Abstract: *Sphingomonas paucimobilis* SYK-6, a bacterium that can grow on 5,5'-dehydrodivanillic acid (DDVA) as a sole carbon source, and call also grow on several dimeric model compounds of lignin. This means that this bacterium has various enzyme systems for getting energy from poor degrading compounds such as lignin. *S. paucimobilis* SYK-6 has the O demethylation systems upon three kinds of substrates; DDVA, syringate, and vanillate. We succeeded in detecting enzyme activity and moleular cloning involved in DDVA spedcific O demethylation and syringate and vanillate specific O demethylation. The biochemical analysis of O demethylation systems revealed that the O demethylation system of DDVA was oxygenase system and that of sringate and vanillate was tetrahydrofolate dependent methyltransferase system. In the genome of SYK-6, the biphenyl specific O demethylase gene and dioxygenase involved in ring fission located in the neighborhood.

2000-107

担子菌におけるダイオキシンストレス応答遺伝子

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Dioxin stress responsible genes from lignin-degrading basidiomycete
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Abstract: To survey the enzymes and genes involved in fungal degradation of dioxin derivatives, the

effect of exogenous dibenzo-*p*-dioxin on extracellular enzyme activities and gene transcription were studied. Lignin peroxidase activity in the culture medium of white-rot fungus *Phanerochaete chrysosporium* increased upon the addition of dibenzo-*p*-dioxin, strongly suggesting the involvement of LiP in the oxidation of this compound. A series of dioxin stress responsible genes were detected using a differential display RT-PCR technique. Several cDNAs of those responsible genes (*FDD-1* to *-6*) were further characterized. The full length cDNA of *FDD-1* was determined and sequenced, indicating that its deduced amino acid sequence showed a high homology to that of quinone oxidoreductase. The expression of this gene was confirmed when dibenzo-*p*-dioxin and catecol were added but not when dibenzofuran was added. The protein encoded by *FDD-1* might play an important role in the reduction of LiP-derived quinone products to the corresponding phenolic compounds for further metabolism.

2000-108

担子菌類の汚染物質分解遺伝子を導入した植物の分子育種と持続的環境修復に関する研究

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Studies on molecular breeding of plants with fungal ability degrades of environmental pollutants and continuous remediation

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Abstract: Plants offer many advantages over bacteria as agents for bioremediation; however, they typically lack the degradative capabilities of specially selected bacterial strains. Innate biodegradative abilities of plants are less impressive than those of adapted bacteria and fungi, but these disadvantages are balanced by the large amounts of plant biomass that can easily be sustained in the field. Transgenic plants expressing microbial degradative enzymes could combine the advantages of both systems. To investigate this possibility, we generated transgenic plants expressing Manganese Peroxidase(MnP), an enzyme derived from *Coliolus versicolor*. In comparison with control, transgenic callus showed high MnP activity.

2000-109

リグニンの*β*-aryl ether 結合の特異的開裂機能を有する新規糸状菌 2BW-1 株の機能及び酵素学的研究

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Detection and characterization of new fungous enzyme catalyzing cleavage of guaiacylglycerol-β- aryl ether bond

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Abstract: Fungus lignin degradation has studied to upspecific degradation from the viewpoint of lignin. The specific degradation of low molecular lignin has been studied in soil bacterium while that of high molecular lignin isn’t yet detected. We forcused in the fungi world that have special extracellular deqvqge fmdnleavage function. In this report, we succeeded isolation the fungus, 2BW-1 strain, that has specifical β-aryl ether cleavge function. This function was observed at the extracellular fraction. In this fraction, thee guaiacylglycerol-β-O-guaiacyl (GOG) was converted into the guaiacylglycerol. It is the new fungus specifical lignin degrading function.

2000-110

耐塩性白色腐朽菌に関する研究（III）：耐塩性白色腐朽菌 MG-60 株が産生する MnP の特性

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Studies on hypersaline-tolerant white-rot fungi. (III). Characterization of manganese peroxidase from a marine fungus MG-60

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Abstract: Characterization of MnPs secreted by a fungus, MG-60 that was incubated at 0% and 3% sea salts concentrations, was reported and the purified MnPs were represented as MnP-0 and MnP-3, respectively, in

this paper. The MnPs were highly tolerant to sea salts and NaCl. The optimum pH and temperature of MnP-0 was 4 and 65ºC, respectively, while, for MnP-3, optimum pH was 3 and optimum temperature was 60ºC.

2000-111

マンガンペルオキシダーゼ活性に影響を及ぼす担子菌菌体外物質について

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The extracellular manganese peroxidase activity-stimulating substances produced by basidiomycetes

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Abstract: Manganese peroxidase (MnP) is an extracellular heme protein produced by wood-rotting and litter-degrading basidiomycetes especilly during secondary metabolism. MnP catatyzes the H2O2-dependent oxidation of phenolic lignin structures. We have focused in extracellular MnP activity-stimulating substances produced by white rot fungi. The best-studied lignin-degrading fungus, *Phanerochaete chrysosporiumum* was cultivated in the liquid medium, and extracellular MnP activity-stimulating substances were prepared. Addition of extracellular substances increased the MnP activity comparing with MnP-MnSO4 system even in succinate buffer. GPC analyses show the
possibility that extracellular substances have absorption at 280nm.

2000-112

ラッカーゼ・1-HBT 系による非フェノール性 β-O-4 型リグニンモデル化合物の分解機構の解析

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岐阜大学農学部

Degradation mechanism of non-phenolic β-*O*-4 ligmin model compound by laccase-1-HBT system

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Abstract: In the previous work, we demonstrated that *Trametes versicolor* laccase catalyzed not only Cα-Cβcleavage, Cα oxidation and β-ether cleavage but also aromatic ring cleavage of a non-phenolic β-*O*-4 lignin model dimer, 1,3-dihydroxy-2-(2,6-dimethoxyphenoxy)-1-(4-ethoxy-3- methoxyphenyl)propane (i), in the present of 1-HBT. This paper reports the incorporation experiments of ^{18}O from H2^{18}O and ^{18}O2 into the degradation products of substrate (i) catalyzed by laccase-1-HBT system. Furthermore, the degradation mechanisms for non-phenolic β-*O*-4 lignin model dimer by this system are discussed.

2000-113

白色腐朽菌 *Ceriporiopsis subvermispora* によるポリイソプレノイドの分解

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Degradation of polyisoprenoids by white rot fungus *Ceriporiopsis subvermispora*

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Abstract: Vulcanized natural rubber sheet was intensively degraded on wood meal cultures by a
selective white rot fungus, *Ceriporiopsis subvermispora*, while *Dichomitus squalens* was not able to decompose the rubber sheet under the same culture condition. *C. subvermispora* also decomposed synthetic polyisoprenoids, styrene-butadiene rubber (SBR) and ethylene-propylene rubber (EP) in addition to natural polyisoprene isolated from natural rubber latex on wood cultures. Structural changes of the fungal treated polyisoprenoids were analyzed.

2000-114

MnP-脂質過酸化複合系による多環式芳香属炭化水素類の酸化

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Oxidation of polycyclic aromatic hydrocarbons by MnP-lipid peroxidation system

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Abstract: We investigate the reaction mechanisms in the oxidation of polycyclic aromatic hydrocarbons by a MnP-mediated lipid peroxidation system. In the system containing 100 mU/ml of MnP, linoleic acid was rapidly consumed and produced active radical species to react with anthraene (AT), consequently a decrease of AT followed to almost a pseudo-first order reaction. The oxidation rates of linoleic acid and AT were not largely affected by the reduction of MnP concentration down to 25 mU/ml in the system. A reaction with very low MnP concentration (2.5 mU/ml) in the system suggests that the MnP-mediated lipid peroxidation to produce active radical species is composed of at least two reactions: the first step is very fast and probably the formation of peroxidized-lipid as intermediates, and the next is the formation of active radical species from intermediates.

2000-115

ペルオキシダーゼ活性を抑制した組換え樹木のリグニン構造

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Lignin chemical structure of transgenic poplar controlling the peroxidase activity
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Abstract: The objective of our research was to form a super tree using new biotechnological and genetic engineering techniques. The primary aim was to produce a tree with a lower lignin content by controlling lignin biosynthesis genes using antisense RNA. The isolation and sequencing of *prxA3a* involved in lignification from hybrid aspen (*Populus kitakamiensis*) was achieved. The transgenic poplars had lower total peroxidase activity compared with that of the control. After peroxidase isozyme analysis by the isoelectric focusing, it was clear that a peroxidase band (pI 3.8) disappeared in the transgenic plants. The lignin content in transgenic plants decreased 20-50% compared with control parts when the potassium permanganate oxidation method was used. A characteristic of the lignin chemical structure in transformants are to have more syringyl units, beta-O-4 structures and condensed units. The decrease of syringyl units and lignin contents in the primary xylem tissue of transformant (POX27) were also observed by the ultraviolet microscopy.

2000-116

酸化的脱リグニン過程でのβ-O-4 型側鎖構造の変化について

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Change in side-chain of β-O-4 structure during oxidative degradation of lignin
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Abstract: By the ozonation method, erythro and threo (E/T) ratio of arylglycerol-β-aryl ether (β-O-4) structure can be obtained as a ratio between two ozonation products, erythronic and threonic acids. Previously, when wood samples were delignified by NaClO2 treatment, no significant change was observed in E/T ratio of residual lignin. In order to confirm the reason for this, MWL was treated with NaClO2, and changes in side-chain part (β-O-4 structure) of lignin were observed by ozonation method. NaClO2 treated MWL showed almost the same E/T ratio as starting MWL, indicating that delignification reaction proceeded homogeneously during NaClO2 treatment. When MWL was reduced by NaBH4, the yield of both acids increased. This increase is due to the reduction of β-O-4 structure that possessesα-carbonyl structure, but since the reduction of NaBH4 was stereo-preferential, the increase in threonic acid was greater than erythronic acid. When this NaBH4-reduced MWL (red-MWL) was treated with NaClO2, the yields of both acid decreased but not significantly. Probably, oxidatively cleaved aromatics during NaCO2 treatment can still give erythronic and threonic acids by ozonation if they carry β-O-4 structure. But when NaBH4 reduction was conducted after NaClO2 treatment, the yield of ozonation product decreased significantly. The reason for this is probably that the reduction of cleaved aromatics would change these structures into structure that could not produce erythonic and threonic acids by ozonation method. These NaClO2 treatments of red-MWL were conducted in aerobic and anaerobic atmosphere, but no significant difference was observed between these two. At least in this reaction condition, the presence of oxygen does not affect the NaClO2 treatment of (red-)MWL.

2000-117

リグニン中の β-O-4 型側鎖構造の光学活性に関する研究

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Studies on the optical activities of β-O-4 structure in lignin by ozonation method

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Abstract: Erythronic acid and threonic acid were obtained from corresponding *erythro* and *threo* forms of arylglycerol-β-aryl ether structure in lignin by ozonation of Birch wood meal. These acids obtained from lignin keep the stereo structure of side-chain part of β-O-4 ether structure. Erythronic and threonic acids were separated by HPLC and were collected, respectively. The fraction of erythronic acid was subjected to HPLC analysis, and the optical activity was measured by on-line optical rotation detector. The optical activity of threonic acid was also measured. It was confirmed that both *erythro* and *threo* forms of arylglycerol-β-guaiacyl ether structure consist of two enamtiomers. It was strongly suggested that the *erythro* forms of arylglycerol-β-guaiacyl ether structure is optically inactive (enantiomer excess (e.e.)< 3.5%). As to threonic acid, because of the incompleteness of purification, maximum e.e. was rather high but was still less than 10%.

2000-118

熱分解ガスクロマトグラフィーによるシンナムアルデヒドを含むモノリグノール比の解析

園田哲也[*1]、小名俊博[*1]、横井裕明[*2]、石田康行[*2]、大谷　肇[*2]、柘植　新[*2]
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Characterization of monolignol ratio including cinnamaldehydes by pyrolysis-gas chromatography.

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Abstract: It is difficult to determine cinnamaldehyde components in lignin accurately by pyrolysis- gas chromatography (Py-GC) because the secondary formation of cinnamaldehydes are considered to occur from the cinnamyl alcohol components in lignin during pyrolysis. In this work, we examined the compositional analysis of monolignols including cinnamaldehydes in various DHPs and woods using pre-acetylation before Py-GC in order to prevent the secondary formation of cinnamaldehydes during pyrolysis. On the basis of the characteristics peaks on the pyrograms, the monolignol ratios in various DHPs determined with taking cinnamaldehydes into consideration were in excellent agreement with those in the DHP preparation.

2000-119

反応熱脱着ガスクロマトグラフィーによる木材中の抽出成分の迅速分析

横井裕明[*1]、中瀬敬二[*1]、後藤邦佳[*1]、石田康行[*1]、大谷　肇[*1]、柘植　新[*1]、園田哲也[*2]、小名俊博[*2]
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Rapid characterization of wood extractives by reactive thermal desorption-gas chromatography

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[*1] Grduate School of Engineering, Nagoya University, [*2]Forestry Research institute, Oji Paper Co. Ltd.

Abstract: A novel rapid method to characterize wood extractives was developed on the basis of reactive thermal desorption-gas chromatograhy (RTD-GC) in the presence of an organic alkali, tetramethy1ammonium acetate ($(CH_3)_4N^+OCOCH_3^-$;TMAAc). The reactive thermal desorption at 200ºC using TMAAc allowed highly sensitive detection of wood extractives such as fatty acids, steroids and phenols in *Eucalyptus camaldulensis* as their methyl derivatives on the resulting pyrograms without using any cumbersome pretreatments such as solvent extraction. The distribution of fatty acids in extractives was able to estimate by RTD-GC using powdered wood samples as received with relative standard deviations of around 5%. The observed result was in good agreement with that determined using acetone solubles.

2000-特別講演

今後の植物の遺伝子組み換え

林　秀則
愛媛大学理学部

Invited Lecture: Future aspects in genetic engineering of plants

Hidenori Hayashi
Department of Chemistry, Ehime University

Abstract: Gene engineering of stress tolerance in plants is powerful technique which would be helpful to improve the crop productivity and to recover the damaged environment. So far target genes suitable for this purpose have been searched from a variety of organisms and used for plant transformation. In addition to these preexisting gene, more potential genes would be available if we understand the molecular mechanism of each gene product and design proteins having enhanced function by molecular engineering. In this lecture, I will demonstrate an example of gene engineering to enhance the salt tolerance in plant with the gene for synthesis of a compatible solute as well as our approach in the molecular engineering of proteins responsible for heavy metal tolerance in cyanobacteria.

2000-201
MWL 抽出残渣からのリグニンの溶出挙動
廣沢修一、中坪文明
京都大学大学院農学研究科
The behavior of extraction of lignin from wood meal after extraction of milled wood lignin
Shuichi Hirosawa, Fumiaki Nakatsubo
Graduate School of Agriculture, Kyoto University

Abstract: At present, milled wood lignin (MWL) is mainly used to investigate chemical structure of lignin. But the MWL is not representative of the total lignin component. Therefore, elucidation of chemical structure of lignin in the wood meal after extraction of the MWL (WMEM) is important. In this study, lignin in the WMEM was fractionated by extractions with solvents for polysaccharides (hemicellulose, cellulose). Alkali extraction was carried out for the purpose of extraction of hemicellulose and lignin. Then, cellulose and lignin was extracted with LiCl/N, N-dimethylacetamide (DMAc). Determination of lignin contents, nitrobenzene oxidation and sugar analyses were carried out to elucidate behaviors of polysaccharides and lignin during extractions.

2000-202
非フェノール性 α-O-アルキル β-O-4 型シリンギルリグニンモデルのエリスロ・スレオ体の NMR と酸加水分解過程の速度論的解析
岸野正典[*1]、大井　洋[*2]、大原誠資[*3]
[*1] 北海道立林産試験場、[*2] 筑波大学農林工学系、[*3] 森林総合研究所
NMR of erythro and threo forms of nonphenolic α-O-alkyl β-O-4 type syringyl lignin model and kinetics of their acid hydrolysis
Masanori Kishino, Hiroshi Ohi, Seiji Ohara
Hokkaido Forest Products Research Institute, Institute of Agricultural and Forest Engineering, University of Tsukuba, Forestry and Forest Products Research Institute

Abstract: NMR chemical shifts of erythro and threo forms of α-ethyl ether derivatives of veratrylglycerol-β-syringyl ether (VSE: 3-(3,4-dimethoxyphenyl)-2-(2,6-dimethoxyphenoxy)-3-ethoxypropan-1-ol) were assigned on the basis of the kinetics for acid hydrolysis of each diastereomer of VSE into the diastereomers mixture of veratrylglycerol-β-syringyl ether (VS: 1-(3,4-dimethoxyphenyl)-2-(2,6-dimethoxyphenoxy)propane-1,3-diol). One VSE diastereomer eluted earlier by HPLC and the other diastereomer were named VSE$_1$ and VSE$_2$, respectively. The value of z_1 defined as a molar ratio (VS threo to VSE$_1$) at which VSE$_1$ gave VS threo during the acid hydrolysis was found to be 1.000. The value of z_2 for VSE$_2$ giving VS erythro isomer of VS was 0.841. This indicates that VSE$_1$ is the erythro form of VSE. In addition, coupling constants ($J_{\alpha\beta}$) for both VSE$_1$ (erythro VSE) and VSE$_2$ (threo VSE) were 7.0Hz, although those for erythro and threo forms of VS were 3.7 Hz and 7.5Hz, respectively. This indicates that conformations of VSE are changed by introduction of α-ethyl group into VS.

2000-203
遺伝子組換えタバコから得られる木部組織のパルプ蒸解生性
梶田真也[*1]、石藤雅俊[*2]、原　晋一[*2]、川端治彦[*2]、諸星紀幸[*1]
[*1] 東京農工大学大学院 BASE、[*2] 三菱製紙株式会社、
Pulping characteristics of xylem materials from transgenic tobacco phnts
Shinya Kajita, Masatoshi Ishifuji, Shin-ich Hara, Haruhiko Kawabata, Noriyuki Morohoshi
Graduate school of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Mitsubishi Paper Mills Limited,

Abstract: 4-Coumarate:CoA ligase (4CL) is a phenylpropanoid biosynthetic enzyme that converts hydroxycinnamic acids into corresponding CoA esters. Recently, we produced transgenic tobacco plants with a chimeric gene for 4CL. The activity of 4CL and lignin content in the plants were depressed by effect of the introduced gene. In this Study, we found that tobacco chips, the xylem materials from the transgenic plants, was delignified more extensively than those from controls in Kraft pulping process. This result indicates that genetic engineering of lignin biosynthesis with modulation of 4CL activity is an efficient tool for production of new wood materials.

2000-204

HBS パルプ化-RHBS の脱リグニン促進効果

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北海道大学大学院農学研究科

HBS pulping. -Acceleration effect of RHBS on delignification

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Graduate School of Agriculture, Hokkaido University

Abstract: HBS pulping with saving-energy and non-pollution was investigated using aqueous solvents (HBS) with boiling point of about 200ºC. Todomatsu and birch chips were satisfactorily pulped with the pulping process. RHBS recovered only high molecular-weight lignin from spent liquors were reused several times as a pulping solvent, though it consisted of sugars, modified sugars, low molecular-weight lignin and so forth as minor components in addition of a main material HBS. RHBS was a more excellent pulping solvent than pure HBS. The accelerated effect of RHBS on the delignification resulted from aldoses existed in RHBS. Both delignification with HBS and RHBS obeyed two pseudo first-order kinetics, bulk and final phases, respectively. The rate constant of the bulk phase with RHBS was about 1.5 times that with HBS. We name the delignification of lignin with aldoses " aldosolysis ". When heated with aqueous neutral solvent at temperatures of above 200ºC, the depolymerization of lignin takes place by homolysis, though it is accelerated by aldosolysis.

2000-205

HBS パルプ化 —β-*O*-4 モデル化合物の反応（2）—

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北海道大学大学院農学研究科

HBS pulping. - Reaction of β-*O*-4 type lignin model compounds, (2)

Takao Kishimoto, Yoshihiro Sano

Graduate School of Agriculture, Hokkaido University

Abstract: We have been proposed that phenolic β-aryl ethers in lignins are cleaved homolitically via the formation of quinone methide intermediates under HBS (high-boiling solvent) pulping conditions. In order to confirm the delignification mechanism, a phenolic β-*O*-4 type lignin model compound, guaiacylglycerol-β-guaiacyl ether (GG) was treated with 70 wt % aq 1,4-butanediol solution at 180 ºC. Thirteen compounds including 4 monomers, 6 dimers, 2 trimers and 1 tetramer were isolated from the reaction products. Most of those oligomeric products were generated by recombination of phenoxy radicals formed by homolysis of the β-aryl ether. These results support that phenolic β-*O*-4 linkages in lignin are cleaved by radical mechanism under HBS pulping conditions.

2000-206

リグニン芳香核の酸化的開裂に伴う構造変化 —生成する低分子カルボン酸類の起源構造—

角田靖典、新谷博幸、飯塚堯介

東京大学大学院農学生命科学研究科

Structural changes of lignin at oxidative degradation of aromatic rings, -Origin of low molecular weight carboxylic acids

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Abstract: Hardwood kraft lignin was treated with alkaline oxygen (1 mol/L NaOH, 0.3 MPa, 70^{a}C, 8 hours) in H2O, H2O-D2O (1:1) and D2O. ^{13}C-NMR spectra of these three samples indicated the production of many kinds of low molecular weight compounds, especially a lot of carboxylic acids, and introduction of deuterium atoms to their compounds, although quantitative evaluation of each compound or tructure was not accomplished. When alkaline oxygen treated samples in H2O were heated in D2O/NaOD at 70ºC for 8 hours, further structural change of some compounds were indicated by ^{13}C-NMR.

2000-207

酸処理・過酸化水素漂白を用いるクラフトパルプの低二酸化塩素添加・無塩素漂白

大井　洋
筑波大学農林工学系

Non-chlorine bleaching of kraft pulp with small addition of chlorine dioxide using acid treatment and peroxide beaching

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Abstract: Non-chlorine bleaching of hardwood kraft pulp (LUKP) with a small addition of chlorine dioxide was investigated. Acid (A) treatment conducted at pH2-2.5 and 40-80ºC for 30-120min was proposed as the pre-treatment of peroxide (P) beaching. By the A treatment, manganese could be reduced and removed significantly. Kappa numbers of pulp were decreased slightly by the A treatment. The P bleaching at 105ºC could be improved by stabilization of manganese (II) in pulp. Dioxins and coplanar PCBs from LOKP bleaching with a very large excess of chlorine dioxide were determined. Formation of 2,3,7,8-TCDD and PCBs was at a little higher level than the minimum level, but 2,3,7.8-TCDF was distinctly determined. A possibility that an excess of chlorine dioxide may cause TCDFs formation was shown. Then, the sequences using the A-P bleaching and a small addition of chlorine dioxide were developed; O-A-P-D, O-A-P-D-P_2, A-P-A-P-D, A-P-D-P_2-D, A-P-H-D-P_2, and O-A-P-A-P_2, A-P-A-P for totally chlorine free bleaching of LUKP.

2000-208

リグニンの脱水素重合反応に対する分子軌道法によるコンピュータシミュレーション

重松幹二、小林孝行、杉野哲也、棚橋光彦
岐阜大学農学部

Computer simulation by molecular orbital calculation on the dehydrogenative polymerization of lignin

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Abstract: Solvent effect on the dehyrogenative polymerization of lignin was computer-simulated by semi-empirical molecular orbital calculation, MOPAC2000. The simulation was divided into three stages and analyzed; 1) one electron oxidation of monolignols catalyzed by horseradish peroxidase (HRP) analyzed by HOMO energy level, 2) spin density and atomic charge of reactable atoms, 3) transition state and activation enthalpy at radical coupling reaction. All the results of these simulations qualitatively agreed with the experimental results about solvent effect, i.e., the activity of HRP to monolignols, and the increased formation of β-*O*-4 linkage in a nonpolar solvent.

2000-209

分子軌道計算によるフェノール化合物のホルムアルデヒドとの反応性予測

光永　徹[*1]、Anthony H. Conner[*2], Charles G. Hill Jr[*3].
[*1] 三重大学生物資源学部、[*2]USDA-Forest Service, Forest Products Laboratory、[*3]College of Engineering, University of Wisconsin

Predicting the reaction of formaldehyde with phenols by molecular orbital computation

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Abstract: Computational chemistry has been used to study the relationship between the reactivity of a number of phenolic compounds with formaldehyde in an aqueous, alkaline system, and charges calculated for reactive sites on the aromatic ring of the phenolic compound. Atomic- charges foreach phenolic compound were calculated by *ab initio* methods at the RHF/6-31+G level of theory using the ChelpG method. Reaction rate constants were determined from measurements of the concentrations of the phenolic compounds and formaldehyde as functions of time. The charge per reactive site was estimated by summing the charges at all the reactive sites on the phenolic ring and dividing by the number of reactive sites. A strong correlation was observed between the reactivity per reactive site and the average charge per reactive site.

2000-210

超臨界メタノールによる木質系バイオマスの化学変換　—針葉樹と広葉樹の比較—

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Chemical conversion of woody biomass in supercritical methanol. -Comparisons between softwood and hardwood
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Abstract: The supercritical methanol biomass conversion system with batch-type reaction vessel was applied to study the chemical conversion of sugi (*Cryptomeria japonica*) and buna (*Fagus crenata*) woods to useful chemicals. As a result, more than 90% of sugi and buna woods were decomposed and liquefied in methanol for 30min supercritical treatment at 350ºC-43MPa. In addition, buna wood was easier to be liquefied in methanol than sugi at 270ºC-27MPa. It was further indicated for the methanol-insoluble residues that observed differences are mainly originated from intrinsic ones in lignin structure between softwood and hardwood.

2000-211
亜臨界水及び超臨界水による木材の化学変換　—リグニンの分解—
江原克信、坂　志朗
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Chemical conversion of wood by subcritical or supercritical water, -Degradation of lignin
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Graduate School of Energy Science, Kyoto University

Abstract: Chemical conversion of buna wood (*Fagus crenata* Blume) was made in subcritical and supercritical water (>22.1MPa, >374ºC) to study liquefaction mechanism of wood. The treated wood was fractionated into the water-soluble portion, methanol-soluble portion, and methanol-insoluble residues. In this study, a characterization or the lignin was forcused on the methanol-soluble portion. The obtained methanol-soluble porrtion showed to be rich in lignin and more oxidative with more phenolic hydroxyl groups than milled wood lignin (MWL). The alkaline nitrotxnzene oxidation abalyses of the lignin in methanol-soluble and methanol-insoluble portions exhibited a decrease or oxidation products under supercritical water treatment. These observations suggested that a preferential degradation of the ether linkages of lignin ocurred in supercritical water.

2000-212
スギ樹皮のポリエチレングリコール・バイサルファイト法による液化
上野智子、耿　興蓮、芦谷竜矢、親泊政二三、坂井克己
九州大学大学院生物資源環境科学研究科
Liquefaction of sugi (Cryptomeria japonica D. Don) bark by Polyethyleneglycol-bisulfite method
Tomoko Ueno, Xinglian Geng, Tatsuya Ashitani, Masafumi Oyadomari, Kokki Sakai
Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University

Abstract: Polyethyleneglycol-bisulfite treatment was applied to the liquefaction of inner and outer barks of sugi. The optimal temperature of the treatment was 250ºC. The longer liquefaction time resulted in the higher solubilization of inner bark. In the case of outer bark, condensation of lignin and/or tannin appeared to occur during treatments for 60min and longer. The concentration of aqueous sodium bisulfite solution exhibited no influence on solubilization of inner bark. Higher solubilization of outer bark was obtained in higher concentration of the bisulfite solution. This
result suggests that sodium bisulfite caused sulfonation of lignin and condensed tannin which are contained in larger amounts in outer bark than in inner bark.

2000-213
含糖型ポリウレタンの熱的および機械的性質に対するリグニン添加の影響
畠山兵衛[*1]、浅野育洋[*1]、廣瀬重雄[*2]、畠山立子[*3]
[*1] 福井工業大学工学部、[*2] 工業技術院物質研究所、[*3] 大妻女子大学家政学部
Influence of lignin on thermal and mechanical prtoperties of polyurthanes containing saccharides Hyoe Hatakeyama[*1], Y Asano[*1], Shigeo Hirose[*2], Tatsuko Hatakeyama[*3]
[*1]Fukui Institute of Technology, [*2]National Institute of Materials and Chemical Research, [*3]0tsuma Women's University

Abstract: Polyurethane (PU) foams with various lignin and saccharides contents were prepared by changing the ratio between kraft lignin (KL) and molasses (ML) contents in polyethylene glycol (M_w=ca.200). Thermal and mechanical properties of the above polyurethanes (PU's) were investigated by differential scanning calorimetry (DSC), thermogravimetry (TG), simultaneous TG and Fourier-transformed infrared spectrometry (TG-FTIR) and mechanical measurements. Glass transition temperatures (T_g's) of the PU's decreased with increasing KL/ML ratio. However, thermal degradation temperatures (T_d's) increased with increasing KL/ML ratio. The amount of thermal degradation products having characteristic functional groups changed according to the temperature.

2000-214
相分離システムによる草本系リグノフェノール誘導体の誘導
関　範雄[*1]、伊藤国億[*1*2]、船岡正光[*2]
[*1] 岐阜県生活技術研究所、CREST,JST、[*2] 三重大学生物資源学部、CREST,JST
Synthesis of lignophenol derivatives from herbaceous lignocellulosics through phase-separation system
Norio Seki[*1], Kuniyasu Itoh[*1*2], Masamitsu Funaoka[*2]
[*1]Gifu Prefectural Human Life Technology Research Institute, [*2]Faculty of Bioresources, Mie University

Abstract: Lignophnol derivatives were synthesized from various herbaceous lingocellulosics, using phase-separation system that was composed of phenol derivatives and concentrated acid, and their characteristics were investigated. Their yields were higher with mild concentrated acid treatment during this system, compared with that of softwood. Although lignophenol derivatives from herbs had similar basic characteristics to that from woods, some characteristics of which slightly differed with their originating species and woods. These differences would be due to the difference in the network structure of native lignin, the distribution and quantity of ether linkages, and the degree of condensation.

2000-215
両親媒性物質に親和性を示す酢酸リグニンヒドロゲルの調製
西田光邦、浦木康光、佐野嘉拓
北海道大学大学院農学研究科
Preparation of acedc acid lignin hydrogel with affinity for amphiphilies
Mitsukuni Nishida, Yasmitsu Uraki, Yoshihiro Sano
Graduate School of Agriculture, Hokkaido University

Abstract: Acetic acid lignin (AL) prepared by the atmospheric acetic acid pulping of birch was found to form hydrogel by the reaction with polyethylene glycol diglycidyl eher(PE) as a cross-linker under alkaline conditions. In this study, the gelation time and the adsorption ability of the gel to cationic surfactants were investigated to clarify the properties of novel lignin gels. The gel formation depended on amounts of glycidyl group in PE and reaction temperatures. AL hydrogel remarkably adsorbed cationic surfactants with long alkyl chains, but the surfactants with the short chain was not adsorbed. This result suggests that the adsorption was mainly caused from hydrophobic interaction between AL domain of gel and alkyl chain of surfactant.

2000-特別講演
リグニン研究とケナフ栽培利用研究の接点について
鮫島一彦
高知大学農学部
Invited Lecture: About the overlapping points of lignin research and kenaf cultivation and utilization research
Kazuhiko Sameshima,
Faculty of Agriculture, Kochi University

Abstract: Kenaf (*Hibiscus cannabinus* , in some case a variety of *Hibiscus sabdariffa* is included) is a fiber plant which is traditionally used for making rope, bag and other fiber products. It is now, however, widely recognized that kenaf could be one of the possible plants to fight to realize a new fiber production and utilization system for the future in may places in the world. After the industrial revolution wood has been recognized as a fiber plant and used for pulp and paper making and other purposes for large-scale production. It is still true but other fiber plant like kenaf should be utilized as a supplemental fiber for many purposes. Because the population increases, environmental problems and other modern problems could be solved in part by using kenaf as useful plant for human being. Lignin research has been mostly concentrated on wood utilization, but the methods will be adopted to kenaf research and development. It grows fast and have low lignin and silica content, and it might be easier for lignin researchers to find useful methods for kenaf versatile utilization.

2000-P01
リグニンモデル化合物を用いた超臨界メタノールでのリグニンの反応性
辻野潤一郎、河本晴雄、坂　志朗
京都大学大学院エネルギー科学研究科
Reactivity of lignin in supercritical methanol studied with some lignin model compounds
Junichiro Tsujino, Harui Kawamoto, Shiro Saka
Graduate School of Energy Science, Kyoto University

Abstract: Behaviors of lignin in supercritical methanol were studied by using lignin model compounds. As a result, both guaiacyl and syringyl types of aromatic rings and biphenyl type structures were very stable under supercritical condition of methanol. However, β-ether linkage in the phenolic β-*O*-4 model compound was cleaved rapidly into guaiacol and coniferyl alcohol which was further converted to its γ-methyl ether. Non-phenolic β-*O*-4 model compound was, on the other hand, converted initially into its α-methyl ether and further degraded to produce guaiacol. Such a continuous decomposition can suggest that the supercritical methanol treatment is very effective to depolymerize lignin into the lower molecular products. These lines of evidence imply that new phenolic residues of lignin are continuously formed and decomposed repeatedly in supercritical methanol mainly by the cleavage of the dominant β-ether structure in lignin.

2000-P02
非塩素漂白過程における α-カルボニル型リグニン構造の挙動 I. 重水素ラベルとニトロベンゼン酸化を組み合わせた定量法
友田生織、松本雄二、飯塚堯介
東京大学大学院農学生命科学研究科
Formation and degradation of α-carbonyl structure in lignin during chlorine free bleaching, I. Method to estimate the α-carbonyl content in lignin remaining in pulp
Iori Tomoda, Yuji Matsumoto, Gyosuke Meshitsuka
Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: It is generally assumed that α-carbonyl structure is one of the key structures which govern the reactivity of lignin towards non-chlorine bleaching. We developed a method to evaluate the content of α-carbonyl structure in residual lignin without isolating the lignin from the pulp. This method is based on a finding that a deuterium atom introduced to α-position by a $NaBD_4$ reduction of α-carbonyl structure could be retained in aldehyde when nitrobenzene oxidation was applied under mild condition. Under the modified reaction condition of nitrobenzene oxidation, the retention of α-D in a model compound was about 70%.

2000-P03
GC 法によるメトキシル基の定量法の再評価（2）—漂白パルプのリグニンメトキシル基の定量—
後藤仁志[*1]、幸田圭一[*2]、松本雄二[*1]、飯塚堯介[*1]
[*1] 東京大学大学院農学生命科学研究科、[*2] 北海道大学大学院農学研究科
Determination of methoxyl content with GC method.(2). -Determination of lignin methoxyl content in bleached pulp
Hitoshi Goto[*1], Keiichi Koda[*2], Yuji Matsumoto[*1], Gyosuke Meshitsuka[*1]
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Abstract: Several types of lignin model compounds were subjected to HI treatment under various conditions and the yield of methyl iodide was determined. Methyl iodide formation from a compound with electron donating group was faster than that with electron withdrawing group. Not only the iodide concentration but also the acid concentration significantly affected the formation rate of methyl iodide. All these results seemed to be explained well by a hypothesis that the protonation to the oxygen atom of methoxyl group plays a decisive role in the cleavage of this group by HL The ability of carbohydrate as Lewis base to consume acid could partly explain the interfering effect of the carbohydrate on the methyl iodide formation from a model compound, which could be explained also by a consumption of iodide by carbohydrates.

2000-P04

木材炭化に伴う抽出成分の構造変化

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Structural changes of extractives by carbonization of wood

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Abstract: Constitutional analysis of the components extracted with 60% aqueous ethanol from the carbonized or heated (180ºC) white oak (*Quercus alba* L.) wood were investigated. The yield of the extractives from carbonized or heated wood was almost the same with untreated wood, but the color of the solution from treated wood showed light brown and its color became dark brown as the function of time. Gallic acid, syringic acid, vanillic acid, vanillin, syringaldehyde and ellagic acid were contained in the extractives of wood with and without carbonization. On the other hand, the yields of these compounds from carbonized wood meal were 1.6-6.3 times of untreated meal. In addition, 5-hydroxymethylfurfural and sinapaldehyde were formed from treated wood and wood meal.

2000-P05

フェノール性 β-O-4 型リグニンモデル化合物の熱分解

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Thermal degradation of phenolic β-*O*-4 lignin model compounds

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Abstract: Effects of Cαand Cγ structures on the cleavage of the β-ether during thermal degradation of lignin were studied by the reactivity of four phenolic β-*O*-4 lignin model compounds under atmospheric nitrogen at 400ºC for 1 min. As a result, the reactivity varied greatly with the Cα and Cγstructures (Cγ: CH_2OH >> CH_3, Cα: C=O >> $CH_2OH \cong CH_3$). Mechanism of thermal degradation of the β-ether is discussed with these results; Cγ-OH plays an important role in the β-ether cleavage, while neighboring group participation of Cα-OH and a quinonemethide intermediate formed by elimination of this hydroxyl group are not important in the mechanism.

2000-P06

水蒸気圧縮処理による樹液抽出法の開発（II）

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Development of a sap extraction method associated with the compressive molding process, (II)

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Abstract: We have developed a compressive molding process, which converts thinnings or the growth of miscellaneous hardwood species to useful materials. However, sap is disposed of together with wastewater in this process. In this study, utilization of the sap for new industrial materials was investigated. Composition analysis of the sap from white birch, detected the presence of sinapylalcohol and coniferylalcohol. In another study, 5-hydroxymethylfurfural was identified from leaves of Japanese cedar. These compounds will be useful as industrial materials. Furthermore revised settings in the apparatus could yield hydrocarbon compounds which are useful as liquid fuels.

2000-P07

ケナフ靭皮繊維のパルプ化温度に関する研究

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Studies on kenaf bast pulping temperature

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Abstract: The relationship between viscosity and cooking temperature in kenaf bast soda-pulping, at 100ºC, 120ºC, 140ºC was examined. The bleaching after soda-pulping was also tried. Kenaf variety of

Zhejiang-1 grown in Kochi was used as bast sample. The soda-pulping was made after ammonium oxalate pretreatment. Sodium hypochlorite and chlorine dioxide were used for bleaching experiment. Yield, Kapper number, viscosity, and brightness were measured. Kappa number didn't decrease much at 100ºC and 120ºC but started to decrease at 140ºC. In contrast viscosity decreased proportionally to cooking temperature increase. In bleaching, sodium hypochlorite showed maximum brightness, but that of chlorine dioxide increased proportionally to the dosage.

2000-P08

HBS パルプ化　—回転式オートクレーブによるシラカンバのパルプ化

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HBS pulping-pulping of birchwood by rotating autoclave

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Abstract: HBS pulping of birch wood with PG in a rotating autoclave was carried out at 200ºC, for 1 to 2 h. Pulping spent liquors were separated into lignin and RPG. RPG consisted of low molecular lignin products, ugars and modified sugar products in addition to PG as a main material. The results on the yields of pulp, pulp residual lignin (KL) and lignin showed that PG and RPG were good pulping solvents corresponding to butanediols (BDOL) and RBDOL, though RPG and RBDOL were better solvents tha PG and BDOL. The strength properties of PG pulp were inferior to those of corresponding kraft pulp, but comparable to those of BDOL and other organosolv pulps.

2000-P09

常圧酢酸法によるバイオマス成分の効率的総合利用

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Total utilization of biomass with efficiency with atmospheric acetic acid process.- Separation of birch components using a large-scale extractor

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Abstract: Birch was separated into wood, outer bark and inner bark fractions. Ten kg of chips prepared from the wood fraction was refluxed with 90% AcOH containing a small amount of H_2SO_4 for 1-3 h by use of all extractor of 100L capacity to be divided into pulp, lignin and water solubles. Xylose was isolated and purified from the water solubles to convert to xylitol. The outer bark faction (3.4 kg) was refluxed with absolute AcOH by the same extractor to extract betulin.

2000-P10

樹皮のグリコール—バイサルファイト法による液化反応の解析

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Reaction of liquefaction of bark by glycol-bisulfite method

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Abstract: Liquefaction of bark by glycol-bisulfite method was analyzed. Especially, conversion of polyphenolic components under the liquefaction condition was examined. Catechin as tannin monomer and quebracho tannin were treated with ethylene glycol and aqueous sodium bisulfite at 250ºC. The products were extracted by water and ethyl acetate. Catechol was detected as a common product by GC-MS analysis of the ethyl acetate soluble parts obtained from the treatment of catechin and quebracho tannin. From IR spectra, it was assumed that solvent-insoluble precipitate was polymerization products of low molecule phenolic compounds like catechol.

2000-P11

酢酸リグニン-古紙混合物の押し出し成形と活性炭化

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北海道大学大学院農学研究科

Extrusion molding of a mixture of acetic acid lignin and waste paper, and its conversion to activated carbon moldings

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Abstract: An aim of study is to prepare activated carbon (AC) moldings, such as pellet and sheet, from the mixture of acetic acid lignin and waste newspaper continuously. The continuous molding of the mixture even with 10% of the infusible newspaper was carried out by extrusion molding using single screw extruder equipped with mono hole nozzle in a diameter of 3 mm and T-die as dice for preparing long pellet and sheet, respectively. Such moldings were converted to AC moldings by steam activation. The sheet prepared by the extruder required longer activation time than that by thermal compression method to produce the AC with more than 900 m^2/g of specific surface area.

2000-P12

免疫法によるスギ心材成分の標識 3. 抗アガサレジノール血清の認識選択性

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Immunolabeling of heartwood extractives in *Cryptomeria japonica.* 3. Recognition selectivity of anti-agatharesinol serum

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Abstract: Recognition selectivity of the previously prepared anti-agatharesinol serum was examined by competitive inhibition-ELISA using various kinds of wood extractives as competitors. The antiserum had the highest reactivity with agatharesinol among the used extractives. The antiserum was able to differentiate between norlignans according to slight differences in their chemical structures, and reactivities of the extractives other than norlignan were much lower. Competitive inhibition-ELISA using agatharesinol derivatives as well as various norlignans indicated that the antiserum required 1,3-bis-(*p*-hydroxyphenyl)-propene structural unit of agatharesinol for the antigen-antibody reaction and that hydroxylation pattern on one aromatic ring (referred to "B ring") influenced seriously the reactivity.

2000-P13

ペルオキシダーゼアイソザイムの基質認識の差異とシリンギルリグニン生合成における役割

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Substrate utilization toward monolignols of peroxidase isoenzymes and their involvement in syringyl lignin biosynthesis

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Abstract: A peroxidase, SyPO, isolated from the cell walls of poplar callus culture is capable to utilize sinapyl alcohol as substrate most effectively in plant isoperoxidases. In this paper, we compared the ability of SyPO in oxidation and polymerization of sinapyl alcohol to other peroxidases, such as horseradish peroxidase (HRP) and the other isoperoxidase, GPO-2, that was also isolated from the cell walls of poplar callus culture. The results showed that the two peroxidases, HRP and GPO-2 could also oxidize sinapyl alcohol in the presence of coniferyl alcohol, however, these peroxidases could not produce a dehydrogenative polymer from sinapyl alcohol and its oligomer compared to that SyPO could do. The surface plasmon resonance analysis suggests that only SyPO can bind to the oligomer of sinapyl alcohol.

2000-P14

担子菌によるジフェニルエーテル化合物の分解機構

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Fungal degradation of diphenyl ether derivatives

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Abstract: A series of diphenyl ether compounds were effectively degraded by the white-rot fungus, *Coriolus versicolor*. 4-Chlorodiphenyl ether was degraded to produce 4-chlorophenol via the intermediate formation of 4-chloro-4'-hydroxydiphenyl ether. Diphenyl ether was also hydroxylated to form 4-hydroxydiphenyl ether which was further metabolized. Piperonyl butoxide, a typical inhibitor for cytochrome P450, effectively inhibited the hydroxylation of diphenyl ethers. The quantitative recovery of the starting substrates was also confirmed in the presence of piperonyl butoxide, strongly suggesting that the initial step of the metabolic pathways might be the hydroxylation reaction. On the other hand, 4-amino- and 4-hydroxydiphenyl ethers were oxidized by extracellular phenoloxidases.

2000-P15

18SrDNA による有用白色腐朽菌株の同定

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Identification of valuable white rot fungi by 18SrDNA sequences

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Abstract: Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have been a public concern for several decades because of their strong toxicity. We have suggested one white rot fungus, strain MZ-34O, collected from-natural forest in Japan, is able to degrade highly-chlorinated PCDDs and PCDFs. We did not have enough information except that it belongs to white rot fungus. Therefore nucreotide sequences of the small subunit ribosomal RNA gene were used to identify strain MZ-340. Strain MZ-340 was suggested to belong to genus *Ceriporia* with DNA analysis data. Subsequently, morphological observation was done. The observation also supported that strain MZ-34O belongs to genus *Ceriporia*.

2000-P16

遺伝子組み換え微生物バイオリアクターを用いたリグニン芳香核構造からの新規ポリアミド型機能性高分子材料の生産

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The production of the new polyamide type polymer materials from lignin aromatic structure using gene recombination of microorganism

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Abstract: We are currently investigating biotransformation process based on the catabolism of various dimeric lignin compounds by *Sphingomonas pausimobilis* SYK-6, which proceed via protocatechuate meta cleavage pathway. 2-pyrone-4,6-dicarboxylic acid (PDC) is a characteristic intermediate of the protocatechuate meta cleavage pathway. We have prepared the mutant with defective in PDC hydrolase by gene replacement technique (□lig I), by which we have succeeded in producing the PDC in the high yield (ca. 90%) from the low-molecular weight lignin mixture. Since PDC has the unique molecular structure and the polymer made from PDC is expected to have the new function as optical material, we prepared new polyamide type polymer by the interfacial polymerization reaction with hexamethylene diamine.

2000-P17

白色腐朽菌 *Phanerochaete sordida* YK-624 株における ferrireductase 産生について

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Production of ferrireductases by white-rot fungus *Phanerochaete sordida* YK-624

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Abstract: We examined the production of ferrireductase by white-rot fungus *Phanerochaete sordida* YK-624. High level of ferrireductase activity was observed in nitrogen-sufficient culture compared with nitrogen-limited culture. Ferrireductase was produced under the culture containing Fe, although it was

well-known that fcrrireductase by yeast was produced only in Fe-deficient culture. The addition of Mn(IV) to the culture induced the production of both manganese peroxidase and ferrireductase as same level as the addition of Mn(II) did. These result suggest that ferrireductase plays an important role in the reduction of Mn(IV) to Mn(II).

2000-P18

ユリノキの組織培養によるシリンガレジノールの生成

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Formation of syringaresinol in *Liriodendron tulipifera* by callus cultures

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Abstract: Calli were induced from the leaves of young trees of Yurinoki, *Liriodendron tulipifera,* on Gamborg's B5 medium supplemented with 2,4-diclllorophenoxyacetic acid and kinetin, and subcultured on the same medium. High-performance liquid chromatographic analysis of the extractives of calli revealed that the calli produced syringaresinol.

2000-P19

天然からスクリーニングした菌によるダイオキシン類のバイオレメデイエーション

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Bioremediation of dioxins by selected fungi from natural world

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Abstract: Bioremediation of dioxins (PCDD/Fs) contaminated in a paddy soil by fungus PL1 selected by a screening method from the natural world was conducted. The fungus degraded about 90% of the dioxins in the soil when 7% of the fungus was added to the soil and incubated for 30 days. The degradation rate of PCDD/Fs increased with increase in added amount of the fungus. On the contrary, the value of toxicity equivalency quantity (TEQ) in the treated soils deceased with increase in added amount of the fungus because of degradation of PCDD/Fs. Furthermore, the degradation rate of PCDD/Fs in the soil by the bioremediation was improved by addition of a surfactant. The results suggest that bioremediation of dioxins contaminated soils by selected fungi by a screening method is possible.

2000-P20

ダイオキシン分解能を有する菌による焼却灰中のダイオキシン類の分解

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Degradation of dioxins in incinerated ashes by some fungi having ability for degradation of dioxins

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Abstract: Microbial degradation of octachlorodibenzo-*p*-dioxin (OCDD) by three fungi (*Coprinus* sp., *Pycnoporus* sp. and *Lyophyllum* sp.) having ability for degradation of dioxins selected by a screening method from the natural world was conducted in a liquid medium. The three fungi degraded from about 35% to 45% of OCDD for 30 days. And bioremediation of dioxins (PCDD/Fs) in an incinerated ash by three fungi selected by the screening method was conducted in a solid medium. The three fungi degraded from about 40% to 50% of PCDD/Fs. The results suggest that purification of PCDD/Fs in incinerated ashes by the bioremediation with the selected fungi is possible.

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2001-101

TIZ法によるリグニン—糖モデル化合物（DHP−Sugar）の分解

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The degradation of DHP-sugar model compound by the TIZ method
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Abstract: TIZ method is an useful method to cleavage β-*O*-4 bond in lignin quantitatively without any secondary condensation reaction. And in this method, most of α-structure of lignin can be maintained. In this study, at first TIZ method was modified. TIZ method requires three reaction steps (Tosylation, Iodination and Zn treatment). It was found that iodination and Zn treatment could be carried out in one pot. Second, the modified TIZ method was applied to the degradation of DHP- sugar and Loblolly pine MWL. In the degradation products, compound 5 R_2 : Ac) was not found. But, the hydrogenation of the products gave compound 6 R_3: H). It suggested that most of α-structure of β-O-4 structure parts in lignin were substituted.

2001-102

樹幹内におけるβ−O−4型側鎖立体構造の不均一性

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Heterogeneities of *erythro* and *threo* forms of β-O-4 structures in lignin
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Abstract: The ratio of *erythro* and *threo* forms of β-O-4 structures (E/T ratio) and methoxyl group content in tension wood parts of yellow poplar were higher than those in normal wood parts. The distribution of *erythro* and *threo* forms of β-O-4 structures is not homogeneous, and is in fairly good agreement with that of syringyl and guaiacyl units. It was indicated that the methoxyl group is one of the factors which affects the diastereoface-differentiating water addition to quinone methides.

2001-103

GC 法によるメトキシル基の定量法の再評価（3）−メトキシル基解裂反応の機構の解析と共存する炭水化物の影響−

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Determination of methoxyl content with GC method. (3). -Analysis of the reaction mechanism of methoxyl cleavage and the effect of co-existing carbohydrate
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Abstract: Reaction mechanism and possible interfering effects caused by the presence of carbohydrates for the methoxyl determination by hydroiodic acid were investigated. The formation rate of methyl iodide from carbohydrates was quantitatively analyzed. and it was suggested that methyl iodide could arise from carbohydrate even when the carbohydrates did not contain a direct precursor for methyl iodide. It was also confirmed that the presence of carbohydrates depress the formation rate of methyl iodide from lignin methoxyl group. Therefore. the presence of carbohydrates could result both in overestimation and underestimation of methoxyl group depending on the amount of carbohydrates. Hammett plot of substituent effect of side-chain part on the methyl iodide formation suggested SN2cA reaction mechanism for guaiacyl models but no clear relation was observed for syringyl models.

2001-104

TOF-SIMSによるリグニン構造解析

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Analysis of lignin structures by TOF-SIMS

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Abstract: The structure of lignin was investigated by TOF-SIMS. Pine milled wood lignin (MWL) gave some secondary ions which seemed to correspond to guaiacyl lignin fragments. In this study, these secondary ions could be attributed to the typical guaiacyl fragments by labeling experiment of DHP. Deuterium labeled DHP prepared from coniferyl alcohol-[γ-D,D, -OCD_3] was subjected to TOF-SIMS analysis. In addition to two major peaks of C6-C1 structures, some secondary ions with C_6-C_3 structures were also found in the mass spectra of MWL and DHP.

2001-105

熱分解マススペクトロメトリーによるリグニンの分析（II）：腐朽過程における化学構造の差異

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Analysis of lignin by pyrolysis-mass spectrometry, (II). Difference of chemical structure during the decaying process

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Abstract: Sugi woods were decayed by brown-rot fungi (*Fomitopsis palustris)* and white-rot fungi (*Trametes versicolor*). The minute samples(<1pg) from the surface and inner parts of the decayed woods were pyrolyzed at 500ºC for 4s. The products were immediately to a mass-spectrometer and ionized at 20eV. The MS spectra were analyzed by the principal components analysis (PCA). Py-MS and PCA showed (1) the differences in the samples obtained from the surface ant inner parts and (2) the differences rotting process by brown-rot fungi and white-rot fungi.

2001-106

反応熱脱着ガスクロマトグラフィーによる木材中のフェノール性抽出成分の解析

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Characterization of phenolic wood extractives by reactive thermal desorption-gas chromatography

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Abstract: Reactive thermal desorption-gas chromatography (RTD-GC) in the presence of organic alkali was applied to the rapid characterization of phenolic extractives in *Eucalyplus* samples. By the use of tetramethylammonium acetate (TMAAc) as the organic alkali the methyl derivatives of the phenolic acids were expectedly observed on the chromatogram formed through RTD. However, they were concluded to be formed from the extractives together from partial pyrolysis of lignin. This fact suggested that the accurate determination of the phenolic extractives were difficult. Thereupon by using tetrabutylammonium hydroxide (TBAH), the phenolic acids in the extractives without methoxyl group were converted into their perbutyl derivatives, which were clearly discriminated from lignin or the extractives with methoxyl group. Based on the peak intensities of the perbutylated phenolic acids observed on the chromatograms, the contents of the phenolic extractives without methoxyl group were rapidly estimated without using any cumbersome pretreatments of samples such as solvent extraction.

2001-107

Keynote: Monolignol biosynthesis in trees：Recent findings and paths for the future

Vincent L. Chiang
Michigan Technological University

Abstract: We have discovered novel genes that regulate syringyl monolignol biosynthesis in angiosperms and demonstrated that the diversion of guaiacyl monolignol intermediates into syringyl types takes place at coniferaldehyde mediated by coniferaldehyde 5-hydroxylase (CAld5H) , 5-hydroxyconiferaldehyde *O*-methyltransferase (AldOMT) and sinapyl alcohol dehydrogenase (SAD). These discoveries together with our early demonstration that monolignol pathway 4- coumarate: coenzyme A ligase (Pt4CL1) controls lignin accumulation provided us clues to simultaneously increasing lignin S/G ratio and reducing lignin content in trees by concurrent manipulation of the expression of genes encoding these enzymes. New insights derived from

these discoveries to genetic engineering of syringyl lignin in conifers will also be discussed.

2001-108

樹木ポプラにおけるリグニン合成量の遺伝子工学的調節

熊谷大地、川合伸也

東京農工大学農学部

Regulation of lignin synthesis by genetic manipulation from *Populus kitakamiensis*
Daichi Kumagai, Shinya Kawai
Faculty of Agriculture, Tokyo University of Agriculture and Technology

Abstract: It was reported that tabacco LIM protein bound to Pal-box which was a *cis*-acting element for gene expression involved in phenylpropanoid biosynthesis. Thus we have cloned and sequenced a cDNA clone, named *klim*, from young leaves of *Populus kitakamiensis*. The deduced amino acid sequence showed a high identity to other plant LIM proteins which had zinc finger motifs. We also cloned the 5'-flanking region of *klim* from genomic DNA by inversed PCR. We found several zinc finger binding motifs in 1,094 bp of the 5'-flanking region. This motif also exsisted in the 5'-nontranslational region of *klim* cDNA. It suggested that LIM protein might regulate itself.

2001-109

ペルオキシダーゼ過剰発現による除草剤耐性付加

田村　健、寺尾　俊、柳崎　真輝、高橋順子、川合伸也

東京農工大学農学部

Plant peroxidase over-production in tobacco induces herbicide-tolerance
Takeshi Tamura, Shun Terao, Masaki Yanazaki, Yoriko Takahashi, Shinya Kawai
Faculty of Agriculture, Tokvo University of Agriculture and Technology

Abstract: The aspen gene, *prxA3a*, encoding an anionic peroxidase, was over-expressed in transgenic tobacco plants. This gene had been isolated from *Populus kitakamiensis* and characterized that it contributed to lignin-biosynthesis. Peroxidase expression cassette was under the control of CaMV35S promoter. These transgenic plants increased herbicide-tolerance against paraquat, DCMU and atrazin, in leafdisk assay, without the accumulation of lignin. Such resistant plants also had more SOD activities than those of wild-type plants. These indicated that the over-expression of *prxA3a* induced plants the protection from oxidative damage caused by paraquat and DCMU.

2001-P01

高粘度ケナフ靭皮パルプの製造に関する研究（2）シュウ酸アンモニウム前処理とパルプ品質の関係

渡辺大輔、大谷慶人、鮫島一彦

高知大学農学部

Studies on production of high viscosity kenaf bast pulp. (2). Relationship between ammonium oxalate pretreatment and pulp quality
Daisuke Watanabe, Yoshito Ohtani, Kazuhiko Sameshima
Faculty of Agriculture, Kochi University

Abstract: To confirm the importance of ammonium oxalate (Amox) pretreatment before the pulping at normal pressure, the soda pulpings with or without Amox pretreatment were compared. Whole kenaf stem was harvested, and debarked by hand, and air dried. Amox pretreatment was carried out on the bast of 10cm in 0.5% Amox. Soda pulping was performed in 10,15,20,25% NaOH for I hour. The yield of soda kenaf bast pulp without Amox pretreatment was higher than that of Amox pretreated one. This indicates that there exist some material which can be removed by the Amox pretreatment but not in the soda cooking. Viscosity was higher in Amox treated pulp in low NaOH concentrations. Pectin in soda pulp with the Smox pretreatment was about half of that in the pulp without Amox pretreatment. It was confirmed that Amox pretreatment is important if a pulp with lower impurities is required, but high viscosity pulp can be produced without Amox pretreatment although the level of viscosity is a little lower.

2001-P02

クラフトパルプの二酸化塩素漂白におけるダイオキシン類の生成機構

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Mechanism of dioxins formation during chlorine dioxide bleaching of kraft pulp
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Abstract: Kraft pulp and sulfite pulp bleaching mills using chlorine, chlorine dioxide (D) and other chlorinated compounds are under surveillance of the dioxins regulation. The bleaching mills are regarded as "notified establishments" which should pollute water quality. According to it, a limit for emissions of dioxins and PCBs to environmental water from the mills is less than 10pg-TEQ^{WHO1998}/L. The limit should be considered ten times as that of environmental water quality (1pg-TEQ/L). One of questions is that water qualities of process sewers in chlorine dioxide bleaching (ECF) mills are less than the environmental water quality (1pg-TEQ/L), or not. Objectives of this study are to clarify the dioxins level of ECF mill sewers and to know more about mechanism of dioxins formation during chlorine dioxide bleaching of oxygen-delignified hardwood kraft pulp (LOKP) on a basis of the analysis revel for the environmental water quality. Laboratory bleaching was carried out using a mill LOKP(kappa number 9.8), chlorine dioxide from a mill R8 generator and drink water in a laboratory high-share mixer. Active chlorine factors were in the range of 0.14-1.14. The total TEQs are less than 15ppq for the D treated and D and alkali-extracted (E) pulps and less than 0.0057pg-TEQ/L for the D and E spent liquors. ln both cases, 2,3,7,8-TCDD and TCDF were not detected.

2001-P03
アルカリ系蒸解過程におけるリグニン側鎖構造の変化
永谷宏幸、杉元倫子、松本雄二、飯塚堯介
東京大学大学院農学生命科学研究科
Change of lignin side-chain structure during soda- and kraft-pulping
Hiroyuki Nagatani, Tomoko Sugimoto, Yuji Matsumoto, Gyosuke Meshitsuka
Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Glyceric acid was obtained as a predominant product by ozonation of both kraft pulp residual lignin and dissolved lignin. The yield ratio between glyceric acid and tetronic acids (erythronic and threonic) becomes higher with the progress of delignification. Quantitative analysis of the yield of those ozonation products suggested that glyceric acid originates from certain structure(s) which originally present in wood lignin, although structures modified during pulping reaction could also contribute to the formation of this acid.

2001-P04
パルプ残存リグニンの単離とその性状に関する研究　—過ヨウ素酸塩前処理を用いたパルプ残存リグニンの単離—
相見　光、飯塚堯介
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Isolation of residual lignin from unbleached hardwood kraft pulp by a pretreatment with mild periodate treatment
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Graduate School of Agricultural and Life Sciences, the University of Tokyo,

Abstract: lt is very important to elucidate the structural feature of residual 1ignin to understand the reason why it is not removed from pulp during cooking. In order to isolate the residual lignin from pulp, two methods are, at the present, widely used: that is, acidolytic treatment and enzymatic treatment. In this study, we investigated the isolation method of residual lignin by a mild periodate pretreatment. By this treatment, the rings of sugar units in pulp will be opened and the sugar chains will have more flexible conditions. We expect to obtain the residual lignin at higher yield by the subsequent extraction of the treated pulps. When the diazomethane treated pulp was mildly treated with periodate and was extracted with aqueous akali in the presence of $NaBH_4$, about 73% of residual lignin was found to be removed from the pulp. This fact may indicate that the major part of he residual lignin is entrapped in the carbohydrate matrix of pulp.

2001-P05
白色腐朽菌によるケナフおよびシラカバパルプの漂白特性の比較
大前陽子、大谷慶人、鮫島一彦
高知大学農学部

Bleaching. effects of kenaf and shirakaba pulps by white rot fungi
Yoko Ohmae, Yoshito Ohtani, Kazuhiko Sameshima
Faculty of Agriculture, Kochi University

Abstract: Soda-Anthraquinone (AQ) and kraft pulps from kenaf bark, core, or shirakaba were bio-bleached by four white rot fungi, two of them were obtained from the fields and the others were *Phanerochaete chrysosporium* and *Pleurotus ostreatus*. Bleachabilities, such as brightness, kappa number, viscosity of the pulps were investigated in connection with laccase, manganese peroxidase, and lignin peroxiidase activities of each fungus. Bleachability of kenaf core pulp was similar to that of shirakaba pulp, but far from that of kenaf bark pulp. Relationship between bleachability and enzymatic activity was quite dependent upon not only the fungi but also the pulps.

2001-P06

蒸煮・爆砕処理を用いた建築廃材中のリグニンの挙動
前田めぐみ[*1]、樋口暁浩[*1]、佐藤雅俊[*1]、飯山賢治[*2]
[*1] 東京大学大学院農学生命科学研究科、[*2] 東京大学アジア生物資源環境研究センターCharacterization in lignin in waste boards during steam-explosion treatment
Megumi Maeda[*1], Akihiro Higuchi[*1], Masatoshi Sato[*1], Kenji Iiyama[*2]
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Abstract: It was tried to produce binderless board from waste woody materials used in construction using steam explosion procedure. Properties of lignin treated with steam explosion process under various conditions were investigated by chemical analyses and scanning electron microscopy. Hemicellulose was decomposed at higher pressure of steam explosion, and significant amounts of lignin was dissolved in exhaust liquor of steam explosion. S/V ratio of alkaline nitrobenzene oxidation products of lignin in steam explosion pulps was almost constant under conditions used in this study. Mechanical strength of binderless board from steam exploded pulp was also discussed.

2001-P07

酸加水分解リグニンより機能性物質調製の試み（その 2）
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名古屋大学大学院生命農学研究科
Preparation of functional materials from gynnosperm acid hydrolysis lignin, (2)
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Graduate School of Bioagricultural Sciences, Nagoya University,

Abstract: The chemical conversion of sulfuric acid lignin (Klason lignin) (SAL) as an acid hydrolysis lignin into functional materials was investigated. SAL has lower reactivity owing mainly to the high rate of condensed structures and then was phenolized (P-SAL) for its activation. In order to prepare surface-active agents having monosaccharide and carboxyhydroxymethy1 (-CH(OH)COOH) group from P-SAL, phenolized lignin model compounds were treated with xylose in 72% sulfuric acid and glyoxylic acid in alkaline media. The yields of a C-xyloside and products with carboxyhydroxymethyl group were <5% and 75% respectively. The preparation of a surface-active agent with carboxy- hydroxymethyl group from P-SAL is attempted.

2001-P08

PEG・バイサルファイト法により液化したスギ樹皮由来ポリウレタンフィルムの調製
芦谷竜矢[*1]、上野智子[*2]、栗本康司[*3]、坂井克己[*1]
[*1] 九州大学大学院生物資源環境科学研究科、[*2] 福岡女子大学人間環境学科、[*3] 秋田県立大学木材高度加工研究所
Polyurethane film prepared from liquefied sugi bark by PEG-bisulfite method
Tatsuya Ashitani[*1], Tomoko Ueno[*2], Yasushi Kurimoto[*3], Kokki Sakai[*1]
[*1]Graduate School of Bioresource and Bioenviromental Sciences, Kyushu University, [*2]Fukuoka Women's University, Institute of Wood Technology, [*3] Akita Prefectural University

Abstract: Sugi (*Cryptomeria japonica* D. Don) bark was liquefied using PEG-400 and sodium bisulfite at 250ºC. Polyurethane (PU) films were prepared by a solution casting technique after co-polymerization of the obtained liquefied bark and polymeric methylene diphenylene diisocyanate (PMDI) in dichloromethane. Thermal and mechanical properties of the PU films were investigated by thermo gravimetric analysis (TGA),

dynamic mechanical thermal analysis (DMTA) and mechanical measurements. Tensile strengths of the PU films prepared from liquefied sugi bark were 0.2-70 MPa at [NCO]/[OH] ratio = 0.25-1.25. It was suggested from results of DMTA and TGA that components in liquefied bark acted as cross linking agents.

2001-P09

木材及び腐朽材によるクロム(III)および銅(II)の吸着

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Sorption of chromium（III）and copper（II）on wood and biologically decayed wood

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2001-P10

リグニンペルオキシダーゼの電気化学的解析

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Electrochemical analysis of lignin peroxidase

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Abstract: The redox potential of lignin peroxidase (LiP) was measured by a cyclic voltammetry technique. The pyrolytic graphite electrode coated with LiP-embedded tributylmethyl phophonium chloride membrane was utilized. Quasi-reversible electron transfer between LiP and the electrode surface was observed. The redox potential between ferric and ferrous LiP exhibited pH-dependency, indicating that the reductive half-reaction of the LiP occurred as; ferric LiP + $1e^- + H^+ \rightarrow$ferrous LiP.

2001-P11

Phanerochaete crassa WD1694 菌株由来のマンガンペルオキシターゼの精製

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森林総合研究所

Purification of manganese peroxidase from *Phanerochaete crassa* WD1694

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Abstract: Four manganese peroxidase isozymes were purified from the culture fluid of *Phanerochaete crassa* WD1694. The culture filtrate was subjected to DEAE-Sepharose chromatography and DEAE-Toyopearl FPLC, and eluted as a single peak of manganese peroxidase activity. The sample showed a single band at a molecular weight of approximatey 50,000 on SDS- PAGE. The same sample was separated as four bands which had the pI value of 4.50, 4.52, 4.62, and 4.65 on isoelectric phocusing, and all four bands were stained by manganese peroxidase active staining. These results showed that *Phanerochaete crassa* WD1694 produced four manganese peroxidase isozymes which have same molecular weight and different pI values described above.

2001-P12

選択的白色腐朽菌 *Celiporiopsis subvermispora* の菌体外フリーラジカル反応 —NDA による鉄酸化還元の阻害と電荷移動錯体形成

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Extracellular free radical reactions of selective white-rot fungus, *Celiporiopsis subvermispora* - Inhibition effects on iron redox reactions and formation of charge transfer complexes.

Makiko Enoki, Yoichi Honda, Takashi Watanabe, Masaaki Kuwahara

Wood Research Institute, Kyoto University

Abstract: A selective white-rot fungus, *Celiporiopsis subvermispora* is able to decompose lignin without intensive damage of cellulose accompanied by lipid peroxidation. Recently we reported production of three novel lipid-related itaconic acid derivatives by this fungus. Among of them, 1-nonadecene-2,3-dicarboxylic acid (NDA) was analyzed in this report. Electron transfer reactions of Fe(II) and Fe(III) were inhibited by NDA.

NDA formed charge transfer complexes with a quinoid compound originating from phenolic compounds in aqueous solutions. These phenomena suggest that NDA stabilizes Fe(II) and Fe(III) and interacts with oxidation products from phenolic compounds during wood decay by *C. subvermispora*.

2001-P13

白色腐朽菌による土壌中ダイオキシン類の処理の試み —土壌成分の分解への影響について—

好光正豪[*1]、近藤隆一郎[*1]、坂井克己[*1]、東房健一[*2]
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Attempt to treat dioxins in soils by white rot fungi. -Influence of soil components on degradation of dioxins

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Abstract: We demonstrated that polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/DFs) in toluene extracts of the soil were degraded by a white rot fungus *Celiporia* sp. MZ-340. Degradation of a mixture of PCDDs/DFs extracted from the soil by the white rot fungus was examined in a low-nitrogen Kirk medium. The toxic equivalence quantity (TEQ) of the extracts of the soil reduced from 19.0 to 12.4 ng-TEQ/flask, and that of the soil extracts, from which polar organic compounds had been removed by silica gel, reduced from 10.0 to 2.4 ng-TEQ/flask by the treatment for 10 days with the white rot fungus.

2001-P14

白色腐朽菌の有する ferrireductase システムを用いた *in vitro* 系での二酸化マンガン還元

伊藤敬訓、平井浩文、西田友昭
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In vitro reduction of manganese dioxide by ferrireductase system in white-rot fungi

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Abstract: *In vitro* reduction of manganese dioxide by ferrireductase system in white-rot fungi was investigated. The reduction of manganese dioxide by Fe(II)-iron binding compound complex, which occurs at extracellular region of the fungi, was dependent on pH, and Fe(Il)-iron binding compound complex was a good electron donor for the reduction of manganese dioxide compared with Fe(lI) itself. Fe(III)-iron binding compound complex was the best substrate for NADPH-dependent ferrireductase than other ferric chelate. These results suggest that ferrireductase system, including NADPH-dependent ferrireductase and Fe(III)-iron binding compound, is involved in the reduction of manganese dioxide by white-rot fungi.

2001-P15

熱分解におけるリグニン中の各結合様式の反応性

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Reactivity of lignin substructures in pyrolysis of lignin

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Abstract: Reactivity of lignin in pyrolysis was studied at 400ºC focusing on depolymerization, polymerization, carbonization and gasification reactions by using α-*O*-4,β-*O*-4,β-1 and biphenyl types of dimeric lignin model compounds. As a result, the following results were obtained. ① Reactivity for depolymerization varies significantly depending on the model compound structure: α-*O*-4, phenolic β-*O*-4 > non-phenolic β-*O*-4, non-phenolic β-1 > phenolic β-1, biphenyl types of model compounds. ② Carbonization occurs from almost structures via very reactive intermediate without leaving polymerization products soluble in THF. ③ Gasification is not important at 400ºC.

2001-P16

フェノール性 β–*O*–4 型構造の熱分解開裂における α-及び γ-位の水酸基の役割

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Role of Cα- and Cγ-hydroxyl groups on pyrolytic cleavage of phenolic β-*O*-4 type of structure

Haruo Kawamoto, Sunao Horigoshi, Shiro Saka

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Abstract: Role of Cα- and Cγ-hydroxyl groups on pyrolytic cleavage of phenolic β-*O*-4 type of structure was investigated by using a series of dimeric lignin model compounds with regiospecifically deoxygenated structures or regiospecifically methylated structures. As a result, it is revealed that hydrogen bonding between these hydroxyl groups plays an important role in β-ether cleavage, and that this effect is only effective in phenolic structure. These results indicate that conformation of the phenolic βα type of structure is important in the mechanism of the β-ether cleavage.

2001-P17

エレクトロポーレーションによるヒラタケの形質転換

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Genetic transformation of *Pleurotus ostreatus* using electroporation

Manabu Moue, Yoichi Honda, Takashi Watanabe, Masaaki Kuwahara
Wood Research Institute, Kyoto University

Abstract: *Pleurotus ostreatus* is one of the white rot basidiomycetes researched to utilize for biobleaching, bioremediation and catalysis of difficult chemical transformation. In order to elucidate the degrading mechanism of lignin by *P. ostreatus*, it is important to introduce genetic engineering techniques which permit us molecular genetic analysis, such as overexpression of ligninolytic enzymes. In our laboratory, drug resistant marker gene *Cbx*^{R} and transformation system have been developed in this fungus. However, many genetic manipulations, such as gene targeting and functional cloning, are not available if the transformation efficiency is low. We examined transformation of *P. ostreatus* by electroporation aiming at high transformation efficiency.

2001-P18

担子菌のプロテオームデイフアレンシヤルディスプレー解析 —培地成分の発現タンパク質への影響—

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Proteome differential display analysis of basidiomycetes

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Abstract: The white-rot basidiomycete, *Coriolus versicolor*, metabolizes a series of sulfur- containing heterocyclic compounds found in fossil fuels as impurities. In our previous study, certain thiophene and sulfide compounds were degraded by *C. versicolor* more effectively under sulfur- limiting culture conditions, suggesting that the fungus utilizes sulfur compounds as a sulfur source
for growth. To better understand a metabolic system for sulfur compounds and to search for proteins related to the desulfurization, proteome differential display analysis was performed.

2001-P19

ラッカーゼ／1-HBT 系による β-*O*-4 型リグニンモデル化合物の新規 β-エーテル開裂反応について

岩月正人、中川　誠、稲垣真澄、浜辺鮎佳、河合真吾、大橋英雄
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New β-ether cleavage reaction of β-*O*-4 lignin model compounds by laccase/1-HBT system

Masato Iwatsuki, Makoto Nakagawa, Masumi Inagaki, Ayuka Hamabe, Shingo Kawai, Hideo Ohashi
Faculty of Agriculture, Gifu University

Abstract: We have studied that the degradation mechanism of non-phenolic β-*O*-4 lignin model compounds by laccase/1-HBT system. In the previous work, we proposed new mechanisms for the formation of Cα-Cβ cleavage product via benzylic radical. In this study, we further investigated the incorporation experiments of ^{18}O from $^{18}O_2$ into the degradation products of substrate (1) and (2) catalyzed by laccase/1-HBT system respectively. The results suggest that a novel β-ether cleavage reaction is caused by laccase/1-HBT system.

2001-P20

植物細胞壁成分の安定炭素同位体比に関する研究

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Stable carbon isotope ratios of some plant cell wall components

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Abstract: Stable carbon isotope ratios (δ^{13}C) of some plant cell wall components were determined by an isotope ratio mass spectrometer (IRMS). The carbon of sugarcane (C_4 plant) was isotopically heavier than that of pine and popular (C_3 Plants) significantly, and the carbon of the Klason lignins from all the species were about 2.6-3.7 ‰ lighter than that of the α-celluloses. These results showed the same tendency as the previous reports1) 2). Although δ^{13}C of components of each tissue in sugarcane were also determined, the reproducibility was not enough. Further precise measurements are needed to make differences between the tissues clear.

2001-P21

コニフェリルアルコールの脱水素重合中に生成するシリンギル核

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Syringyl units generated during the polymerization of coniferyl alcohol

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Abstract: Syringyl (S) and *p*-hydroxyphenyl (H) units were detected in addition to guaiacy1 (G) unit in thioacidolysis products obtained from the DHP prepared from only coniferyl alcohol using a peroxidase-H_20_2 System. To determine the DHP at the dimer level, we analyzed thioacidolysis products of the DHP and detected dimers of G-G, S-G, S-S and H-G types.

2001-P22

カプール（*Dryobalanops* spp.）心材の抗う蝕活性成分の検索

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Anti-dental caries active compounds of kapur (*Dryobalanops* spp.) heart wood extracts

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Abstract: The inhibitory effects of 22 species of wood extracts on the glucosyltransferase (GTase) activity were investigated. Kapur (*Dryobalanops* spp.) heart wood extracts showed inhibited

GTase activity more effectively than any other species. The results obtained by the Folin-Denis method for the determination of total phenol contents, vanillin-HCl method to determine flavanol contents and protein adsorption by using BSA suggested that the active fractions contained hydrolyzable tannin like component. The main components which inhibit GTase activity in kapur were probably ellagitannins, because a large amount of ellagic acid was released by acid hydrolysis. Furthermore, these components exhibited antioxidative activity in a rabbit erythrocyte membrane ghost system.

2001-P23

分子軌道計算を用いたポリフェノールの反応性の解析 —フラボノイド類の付加縮合反応速度と分子軌道計算値との相関性—

渡辺泰高、光永　徹
三重大学生物資源学部

Reactivities of polyphenols with formaldehyde by Molecular Orbital Computation. —Correlation additional condensation rates of flavanoids and the parameters calculated by molecular orbital method

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Faculty of Bioresources, Mie University

Abstract: Molecular Orbital Computation for flavonoids, (+)-catechin and taxifolin, has been used to study the relationshjp between the calculated electrostatic charges at the carbons existed Highest Occupied Molecular Orbital (HOMO) and the reaction rate of hydroxymethylation with formaldehyde. Electrostatic charges (q) of several kinds of flavonoids were calculated by semi- empirical methods at the AM1 and PM3 and *ab initio* methods at RHF/3-21G level of theory. The rate (k) of flavonoids consumption were determined by HPLC. When q were plotted against logarithm of k in these flavonoids, phenol, resorcinol and phloroglucinl, high correlation (R^2=0.92) was obtained.

2001-P24

マタイレジノールの 5 位水酸化過程に関する考察

大須賀優夫、鈴木視番、木原智仁、榎本慎一、河合真吾、大橋英雄、小山博之、原　徹夫
岐阜大学農学部

5-Hydroxylation of matairesinol in syringyl lignan biosynthesis

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Abstract: We have studied on the biosynthesis of syringyl lignans in *Thuja* species. In the previous work, we suggested that matairesinol is the possible intermediate on the biosynthetic pathway of syringyl lignans. In this study, we report the feeding experiment of [7, 7-$^{2}\mathrm{H}_{2}$, 3'-O$\mathrm{C}^{2}\mathrm{H}_{3}$]matairesinol into *T. occidentalis* young shoot. The results indicated for the first time that matairesinol was converted into thujaplicatin. Last of all, we show a preliminary experiment for the detection of matairesinol 5-hydroxylase gene.

2001-110

ペルオキシダーゼ遺伝子を抑制した形質転換ポプラの化学的・組織化学的解析

李　並紅、太田祥弘、梶田真也、諸星紀幸
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Characterization of transgenic aspens inhibited by a peroxidase gene

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Abstract: To study the down-regulation of specific peroxidase involved in lignin biosynthesis and its correlation with lignification, an anionic peroxidase gene, prxA3a was transferred into its original host, hybrid aspen P. kitakamiensis (*P. sieboldii* X P. *gradidentata*) under the control of the original promoter of prxA3a. Twelve transformed lines were regenerated and confirmed by PCR and Southern blotting. Enzyme assay showed that both total peroxidase activity and prxA3a specific activity were decreased in most transgenic lines as compared to control plant. In addition, difference in lignin content and structure was observed between transformants and control aspen. Furthermore, histochemical analysis revealed that suppressed lignification in the secondary xylem was the result of down-regulated peroxidase expression. These results indicated that it was achievable to develop genetically improved woody plant.

2001-111

担子菌カワラタケの環境汚染物質分解酵素遺伝子（*mnp,lac*）を導入した植物の分子育種と持続的環境修復に関する研究（2）

池田成一郎[*1]、園木和典[*1]、飯村洋介[*2]、早川敏夫[*3]、金原和秀[*3]、梶田真也[*1]、片山義博[*1]
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Studies on molecular breeding of plants with ability of MnP, Lac derived from *Coliorus versicolor* degrade environmental pollutants and continuous remediation

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Abstract: Remediation methods for environmental pollutants such as physical & chemical treatment and bioremediation have been experimentally tested. However, these methods have some problems; these are impractical in view of cost efficiency of hazardous chemicals accumulated at low levels in the environment or becomes labored as the area of contamination expands. Meanwhile, plant call be grown independently taking nourishment from the sun, water, and inorganic ions, and can be cultivated extensively by controlling seeds. Because of this, plants have attracted attention as a method for long-lasting environmental decontamination. And, we have attempted to degrading hazardous chemicals directly using transgenic plants into which Mn-Peroxidase gene and Laccase gene for degrading hazardous chemicals derived from *Coliorus versicolor* is transfered. If a plant capable of exerting the effect of these enzyme could be prepared, it would be very useful for degrading and removing hazardous chemicals in the environment.

2001-112

微生物の物質変換機能の導入による、植物のフェニルプロパノイド合成系の制御

補永文子[*1]、梶田真也[*1]、園木和典[*1]、上杉幹子[*1]、政井英司[*2]、原田恭[*2]、福田雅夫[*2]、諸星紀幸[*1]、片山義博[*1]
[*1] 東京農工大学大学院 BASE、[*2] 長岡技術科学大学

Manipulation of phenylpropanoid-biosynthetic pathway by genetic engineering with bacterial genes

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[*1]Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, [*2]Nagaoka University of Technology

Abstract: Hydroxycinnamoyl-CoA esters are intermediates of phenylpropanoid biosynthetic pathway and can be precursors of many secondary metabolic compounds such as flavonoids, stilbenes and lignin. A bacterial gene *FerB* isolated from *Sphingomonas paucimobilis* SYK-6 encodes feruloyl-CoA hydratase/lyase. This enzyme can catalyze the reaction step for conversion from hydroxycinnamoyl-CoAs to corresponding hydroxybenzaldehydes. We tried to express this gene in tobacco and hybrid aspen plants by genetic engineering in aim to biosynthesize beneficial phenolic compounds in vivo. The transgenic plants showed activities to produce hydroxybenzaldehydes.

2001-113

ペルオキシダーゼアイソザイムの基質認識とシリンギルリグニン生合成の役割

佐々木慎弥[*1]、堤　祐司[*1]、西田友昭[*1]、光永　徹[*2]
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Substrate utilization toward monolignols of peroxidase isoenzymes and their involvement in syringyl lignin biosynthesis

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Faculty of Agriculture, Shizuoka University, Faculty of Bioresource, Mie University

Abstract: A peroxidase, SyPO, isolated from the cell wall of poplar (*Populus alba* L.) callus culture is capable to utilize sinapyl alcohol (Salc) as substrate most effectively in plant isoperoxidases. SyPO polymerized sinapyl alcohol-oligomer (Salc-oligomer) and sinapyl alcohol, producing a polymer of greater molecular weight. In contrast, horseradish peroxidase (HRP), which is specific to coniferyl alcohol (Calc), produced sinapyl alcohol diners, rather than catalyzing polymerization. Adding coniferyl alcohol as a radical mediator in the HRP-mediated reaction did not result in Salc-oligomer polymerization.

2001-114

シナップ酸に活性を有する 4-coumarate : coenzyme A ligase の検索

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[*1] 静岡大学農学部、[*2] 名古屋大学大学院生命農学研究科

Screening of 4-coumarate: coenzyme A ligase utilizing sinapic acid as substrate

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Faculty of Agriculture Shizuoka University, Graduate School of Bioagricultural Sciences, Nagoya University

Abstract: The conversion of sinapic acid to sinapoyl CoA was confirmed by an enzyme assay using ^{14}C-labeled sinapic acid and crude enzyme preparation from *Robinia pseudoacacia* L.. This and previous results indicate that *R. pseudoacacia* has a biosynthetic pathway for sinapyl alcohol via sinapic acid. Fractionation of the crude enzyme using a Mono Q column resulted into the resolution of two 4CL isoformes. The molecular weight of the one major 4CL fraction was estimated to be ca. 64kD by SDS-PAGE followed by the treatment with 4CL-specific antiserum. This partially purified 4CL showed high activity with *p*-coumaric acid but very low with sinapic acid and ferulic acid. Isolation of the 4CL isozyme active against sinapic acid in *R. pseudoacacia* is ongoing.

2001-115

特別講演

茶の香気生成機構の研究から植物グリコシダーゼ研究の新展開へ

坂田完三
京都大学化学研究所

Invited Lecture: New research developments of plant glycosidases from studies on molecular basis of aroma formation during tea manufacturing
Kanzo Sakata
Institute for Chemical Research, Kyoto University,

Abstract: We have clarified the molecular mechanism of floral tea aroma formation during tea manufacturing. Floral aroma such as geraniol, linalool, etc. are present mainly as β-primeveroside (6-*O*-β-D-xylopyranosyl-β-D-glucopyranosides in fresh tea leaves), which are hydrolyzed by a disaccharide specific glycosidase, β-primevrerosidase, to aglycons (aroma compounds) and primeverose. The glycosidase shows a very high substrate specificity to β-primeverosides. Gene cloning of the glycosidase shows very high homology in its amino acid alignment to that of amygdalin hydrolase (57 %). We also have succeeded in synthesis of new type of glycosidase inhibitors (glycosyl amidines), which can be easily synthesized from each sugar without protecting hydroxy groups. Each glycosyl amidine shows very high selective and competitive inhibitory activity against its corresponding glycosyl hydrolase. A successful application for affinity chromatography is shown.

2001-116
特別講演
リグノセルロースの利用 —現状と将来
畠山兵衛
福井工業大学工学部
Invited Lecture: Utilization of lignocellulosics, —Present and future
Hyoe Hatakeyama
Faculty of Engineering, Fukui University of Technology

Abstract: This paper reviews liquid crystals, high performance polymers and environmentally compatible polymers that have been derived from saccharides and phenolic compounds. Liquid crystals were synthesized from 4-hydroxylphenyl, guaiacyl and syringyl derivatives which are obtainable from lignin. Polymers such as polyurethanes containing saccharide and lignin structures were also synthesized. Polycaprolactone derivatives were synthesized from lignin, cellulose and cellulose acetate. Thermal and mechanical properties of the above saccharide- and lignin- derivatives were studied by differential scanning calorimetry, thermogravimetry, thermogravimetric infrared spectroscopy (TG-FTIR) and mechanical measurements.

2001-201
Anthricus sylvestris におけるシリンギル型リグナン生合成経路について
榊原紀和、鈴木史朗、梅澤俊明、島田幹夫
京都大学木質科学研究所
Syringyl type lignan biosynthesis in *Anthriscus sylvestris*
Norikazu Sakakibara, Shiro Suzuki, Toshiaki Umezawa, Mikio Shimada
Wood Research Institute, Kyoto University

Abstract: Feedirq experiments with *Anthriscus sylvestris* have indicated that thujaplicatin, 5-methylthujaplicatin, 4, 5-dimethylthujaplicatin are good precursos of the syringyl type lignan yatein. Furthermore, *Anthriscus sylvestris* cell-free extracts catalyzed *O*-methylation of several lignans including thujaplicatin and 5-methylthujaplicatin.

2001-202
熱帯産イネ科飼料植物の消化性と細胞壁化学構造
樋口暁浩[*1]、飯山賢治[*2]
[*1] 東京大学大学院農学生命科学研究科、[*2] 東京大学アジア生物資源環境研究センター
Structural feature of indigestible wall components of tropical forage grasses
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Abstract: Setaria grass (*Setaria sphacelata* (Schmach.) Stapf & Hubbard ex M.B. Moss) and Guinea grass (*Panicum maximum* Jacq.) as tropical forage grass were investigated for the relation- ship between cell wall structure and their digestibilities. *In vitro* cell wall digestibility (IVCWD) was highly correlated with hydroxycinnamic acid content, especially indigested hydroxycinnamic acid content. This result suggests that indigestible cell wall contain high amount of covalent association between lignin and wall polysaccharides (LCC) through hydroxycinnamic acids. Generally, parenchyma cell in grass stems was easily digested. However, Setaria and Guinea grasses have indigestable parenchyma.

2001-203

カカオ（*Theobroma cacao* L.）種皮の導管及び非導管組織中のポリフェノールの差異

Byung–Yeoup Chung[*1]、飯山賢治[*2]
[*1] 東京大学大学院農学生命科学研究科、[*2] 東京大学アジア生物資源環境研究センター

Differences in accumulated polyphenolic compounds between vascular bundles and non-vascular bundles of Cacao（*Theobroma cacao* L. ）hull

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[*1]Graduate School of Agricultural and Life Sciences, the University of Tokyo, [*2]Asian Natural Environmental Science Center, the University of Tokyo

2001-204

ラット尿中に存在する DHP 由来のファイトエストロジェン

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Phytoestrogens found in the urine of a rat after oral administration of DHP

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Abstract: Two groups of hormone-like diphenolic phytoestrogens, lignans and isoflavonoids, are exist in human body fluids, and have gained increasing interest because of their possible cancer protective properties. The phytoestrogenic lignans are called mammalian lignans. The two major mammalian lignans, enterodiol and enterolactone, are thought to be the products of colonic bacterial metabolism of the plant precursors secoisolariciresinol and matairesinol. However little is known about, the biotransformation of these compounds. And the possibility that lignin in the dietary fiber might be converted into mammalian lignans has been considered. In order to clarify whether lignin is biotransformed to mammalian lignans, lignin model compound, DHP prepared by endwise polymerization of coniferyl alcohol was administrated to the female Wistar rat and the urine was analyzed by GC-MS. Enterodiol and enterolactone were detected, which were not detected in the control urine. This is sufficient to show the possibility that DHP could be converted into mammalian lignans.

2001-205

無機系粒子分散型ポリウレタン系ジオコンポジットの機械的性質

馬渕将人、畠山兵衛
福井工業大学工学部

Mechanical properties of geocomposites of the polyurethane system containing lignin

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Fukui University of Technology

Abstract: Polyurethane (PU) geocomposites were prepared from a mixture of lignin, polyethylene glycol (PEG) (Mw=ca.200) and silicic sand. The content of lignin in PEG was changed from 0 to 90%. Mechanical properties of the above PU geocomposites were investigated by mechanical measurements. In the kraft lignin (KL)-PEG200-polyphenyl polyethylene polyisocyanate (MDI) system and in the lignosulfonate (LS)-PEG200-MDI system, the permeation distance of PU into silicic sand increased with increasing lignin contents. However, a maximum stress of the PU geocomposites decreased with increasing lignin contents.

2001-206

リグノスルホン酸含有硬質ポリウレタンフォームの調製と物性

浅野育洋[*1]、畠山兵衛[*1]、畠山立子[*2]
[*1] 福井工業大学工学部, [*2] 大妻女大学家政学部

Preparation and properties of lignosulfonate-based rigid polyurethane foams

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Abstract: Rigid polyurethane (PU) foams were prepared from lignosulfonate (LS) dissolved in diethylene glycol (DEG), triethylene glycol (TEG) or polyethylene glycol (Mw=200:PEG200) by the reaction with polyphenyl polymethylene polyisocyanate (MDI). Thermal and mechanical properties of the above polyurethanes (PU's) were investigated by differential scanning calorimetry (DSC), thermogravimetry (TG), and compression tests. Glass transition temperatures (T_g's) of the PU's from the LS-PEG200-MDI system increased slightly with increasing LS content. However, T_g's of the PU's from the LS-DEG-MDI system did not show obvious change with increasing LS content.

2001-207

リグニンを原料とするエステル系エポキシ樹脂の合成と熱的性質
廣瀬重雄[*1]、畠山兵衛[*2]
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Synthesis and thermal properties of ester-epoxy resins from lignin
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Abstract: Alcoholysis lignin (AL) was dissolved in ethylene glycol and the obtained mixture was reacted with succinic anhydride to form a mixture of ester-carboxylic acid derivatives (AL-polyacid, ALPA). Ethylene glycol-polyacid (EGPA) was also prepared from ethylene glycol. The obtained mixture of ester carboxylic acid derivatives was reacted with ethylene glycol diglycidyl ether in the presence of catalytic amount of dimethylbenzylamine to form ester-epoxy resins. The curing reaction was analyzed by Ozawa's method using differential scanning calorimetry (DSC). The activation energy (E) of curing reaction in the initial step was found to be ca. 83 kJ/mol. The molar ratios of epoxy groups to carboxylic acid groups ([EPOjN]/[AA] ratios, mol/mol) were varied from 0.8 to 1.3. The contents of ALPA in the mixture of ALPA and EGPA (ALPA content) were also varied from 0 to 100 %. Thermal properties of epoxy resins were studied by DSC and thermogravimetry (TG). Glass transition temperatures (T_g's) of epoxy resins showed a maximum value of -11.5 ºC when [EPOXY]/[AA] ratio was 1.1. T_g's increased with increasing ALPA contents suggesting that lignin acts as a hard segment in epoxy resin networks. Thermal degradation temperatures (T_d's) of epoxy resins slightly decreased with increasing ALPA contents.

2001-208

アルカリ性酸素処理に伴うリグニンの赤外吸収スペクトルの変化
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The changes in infrared spectra of lignin by alkaline oxygen treatment
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Abstract: Various oxidizing agents were applied for bleaching sequence of kraft pulp. Oxygen delignification under alkaline condition which is employed by many plants is important process for pulp bleaching. Structural changes of lignin during oxygen delignification stage are, however, not clarified yet in detail. In this study, softwood and hardwood kraft lignins were treated with alkaline oxygen (1M NaOH, 0.3MPa, 70ºC) for 0.5-8.5 hours, and the reaction solutions were analyzed by IR spectroscopy with ATR (Attenuated Total Reflection) methods. The changes in spectra depending on reaction time indicated that aromatic rings with high reactivities to oxygen were almost cleaved until 2.5 hours of reaction, while increase of absorbance due to carboxyl group continued to 8.5 hours of reaction. Spectral changes were observed when pH of the reaction solution of softwood kraft lignin treated for 3.0 hours was increased from 9.4 to 12.2, which should be caused by the difference of degree of dissociation of phenolic hydroxyl groups.

2001-209

酸素漂白過程におけるフェノール類の酸化反応速度
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東京大学大学院農学生命科学研究科
Model studies on kinetics of phenol oxidation during oxygen bleaching
Tomoya Yokoyama, Yuji Matsumoto, Gyosuke Meshitsuka
Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Several phenolic compounds were subjected to oxygen-alkali treatment, and their degradations were analyzed in detail by applying a novel formula_ This formula was established by two considerations. One was that the degradation of phenolic compounds should be expressed by the sum of two reactions; one of which is caused by molecular oxygen and the other by active oxygen species. The other consideration was that the degradation of phenolic compounds should be written by a pseudo-first-order reaction in which the rate constant $k_{obs}(t)$ is dependent on reaction time. By arrangements, $k_{obs}(t)$ was shown as a hyperbola. The contribution of active oxygen species to the degradation of phenolic compounds is visualized by illustrating $k_{obs}(t)$. The higher the temperature is, the more active oxygen species contribute to the degradation of phenolic compounds. The extrapolation of $k_{obs}(t)$ to the beginning of the reaction gave an initial pseudo-first- order reaction rate constant $k_{obs}((initial)$. The reaction between phenolic compounds and molecular oxygen without any influence of active oxygen species can be elucidated by using $k_{obs}((initial)$. As expected, $k_{obs}((initial)$ is dependent on functional groups, which indicates that their electronic effect on the aromaticπelectron system provides the reaction rate of phenolic compounds with molecular oxygen.

2001-210
非塩素系漂白過程における α−カルボニル型リグニン構造の挙動 II. 定量法の確立とそのパルプ残存リグニンへの適用
友田生織、松本雄二、飯塚堯介
東京大学大学院農学生命科学研究科
Formation and degradation of α-carbonyl structure in lignin during chlorine free bleaching, II. Method to estimate the α-carbonyl content in lignin remaining in pulp
Iori Tomoda, Yuji Matsumoto, Gyosuke Meshitsuka
Graduated School of Agricultural and Life Science, the University of Tokyo

Abstract: When guaiacylglycerol-β-guaiacyl ether carrying deuterium at α-methin position (GGα-D) was subjected to nitrobenzene oxidation under the usual reaction condition, the retention of deuterium in the formyl group of the reaction product (vanillin) was quite low because of the D-H exchange during the reaction. The D-H exchange could be suppressed by employing LiOH or $Ba(OH)_2$ as an alkali during nitrobenzene oxidation. This finding was applied to the semi-quantitative analytical method of lignin α-carbonyl structure, which consists of successive $NaBD_4$ reduction of α-carbonyl structure and nitrobenzene oxidation. Experiments using α-carbonyl enriched MWL (DDQ treated MWIJ) and its H_2O_2 treatment product revealed that the increase and the decrease of α-carbonyl structure in lignin could be successfully analyzed by this method.

2001-211
酸処理・過酸化水素漂白を用いるクラフトパルプの無塩素漂白
大井　洋、池田　努
筑波大学農林工学系
Non-chlorine bleaching of kraft pulp using acid and hydrogen peroxide
Hiroshi Ohi, Tsutomu Ikeda
Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: Chlorine dioxide is most popular chemical to convert the bleaching from chlorine system to ECF system. But usually over three times chlorine dioxide need to get the same result that of chlorine system. We discussed about decreasing chlorine dioxide during ECF and non-chlorine bleaching using acid, ozone and hydrogen peroxide. Kappa number 9.4 LKOP contained hexeneuronic acid that was equivalent to kappa number 2.3. After acid treatment and ozone bleaching kappa number decreased to 2.9. But about 26% hexeneuronic acid that was equivalent to kappa number 0.6 still existed in pulp.

2001-212
On-line Kappa number determination in sulfite pulping by visible spectroscopic measurements on spent liquor
Yimin Xie, Wenhao Shen, Huanbin Liu
South China University of Technology

Abstract: This paper presents a method of on-line measurement of Kappa number with visible spectroscopy during batch sulfite cooking. It was discovered that the absorption of the spent liquor from Masson's pine in 460-580nm wave range resulted mainly from lignin-sulfonate with high molecular weight (MW>30KD) and that Kappa number maintained a linear relationship with the absorbency of the spent liquor within the wave range. Mathematical models of on-line Kappa number determination with visible light of 460-580nm wavelength were developed by chemometrics for batch sulfite cooking. These models had high learning and prediction precision. Their relative errors were less than 1.5 Kappa number.

2001-213

HBS パルプ化　—溶媒の安定性とパルプの漂白性
佐野嘉拓、オリギル、梶本純子
北海道大学大学院農学研究科
HBS pulping- sabilization of solvents and bleachability of HBS pulp
Yoshihiro Sano, Aorigele and Junko Kajimoto
Graduate School of Agriculture, Hokkaido University

Abstract: We has reported in the earlier work of this series that not only hardwood and nonwood, but softwood can be pulped at elevated temperatures and low pressure by HBS pulping process using low-volatile solvents (HBS) with the boiling pint of about 200ªC. One HBS introduced into pulp process has to be recovered quantitatively from spent liquors to be used repeatedly as pulping solvents, so the stability of HBS to heat was investigated. Also, in order to prepare complete- bleached pulp for paper-grade, functional cellulose and biopolymers, the bleachability of HBS pulps was studied. The results showed that the pulps were easily bleached by ECF sequence and TI of each pulp was improved significantly by bleaching.

2001-214
HBS パルプ化　—リグニンの理化学的性質
長岡秀明、佐野嘉拓
北海道大学大学院農学研究科
HBS pulping. -Physical and chemical properties of lignin
Hideaki Nagaoka, Yoshihiro Sano.
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Abstract: HBS pulping of birch wood with PG in a rotating autoclave was carried out. Spent liquors were separated into lignin and RPG. RPG consisted of low molecular lignin products, sugars and modified sugar products in addition to PG as a main material. The results on the yields of pulp, pulp residual lignin (KL) and lignin showed that PG and RPG were good pulping solvents corresponding to butanediols (BDOL) and RBDOL, though RPG and RBDOL were better solvents than PG and BDOL. Ligmins prepared by HBS pulping with RPG in a rotating autoclave have lower molecular weight, a lower amount of methoxyl groups and a higher amount of phenolic hydroxyl groups than those with PG.

2001-215
酢酸パルプの機能化（2）—パルプ化・漂白および誘導体化を酢酸中で行うシステムの構築—
佐藤大典、辻　洋路、浦木康光、岸本崇生、佐野嘉拓
北海道大学大学院農学研究科
Functionalization of acetic acid pulp, (2) -Construction of the successive system from pulping to derivatization performed in acetic acid
Hironori Sato, Hiromichi Tsuji, Yasumitsu Uraki, Takao Kishimoto, Yoshihiro Sano
Graduate School of Agriculture, Hokkaido University

Abstract: To explore the further application of acetic acid pulp (AP) in addition to the use as chemical pulp, we investigated the production system of cellulose acetate (CA) from wood by the successive treatment of acetic acid pulping, TCF bleaching and acetylation, which were performed in acetic acid. AP with Kappa number 30 and ISO brightness 16 was bleached by ozone (Z) to Z-AP with 1.9 and 48, respectively, and then by the following peracetic acid (Pa) to Z-Pa-AP with 0.6 and 66. The resulting bleached AP could be derivatized to CA with degree of substitution of 2.54 and high solubility in acetone by the conventional acetylation.

2001-216
メソ多孔体へ固定化したマンガンペルオキシダーゼによるバイオパルプ漂白システム
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株式会社豊田中央研究所
New pulp biobleaching system involving manganese peroxidase immobilized in a silica support with controlled pore sizes
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Abstract: Attempts have been made to use manganese peroxidase (MnP) for chlorine-free pulp biobleaching, but they have not been commercially viable because of the enzyme's low stability. We developed a

new pulp biobleaching method involving mesoporous material-immobilized manganese peroxidase from Phanerochaete chrysosporium. MnP immobilized in FSM, a folded-sheet mesoporous material whose pore size is nearly the same as the diameter of the enzyme, had the highest thermal stability and tolerance to H_2O_2. We constructed a thermally discontinuous two-stage reactor system, in which the enzyme (39ºC)and pulp-bleaching (70ºC)reactions were performed separately. After seven cycles of MnP-treatment and alkaline extraction, the brightness of the pulp increased to about 85% within 6h.

2001-217

マンガンペルオキシダーゼを用いたアゾ系反応性染料の脱色

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Decolorization of azo reactive dye by manganese peroxidase system

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Abstract: We investigated the decolorization of azo reactive dye, Reactive Red 120 by white rot fungus *Phanerochaete sordida* YK-624 and its enzyme. The dye (200 mg/l) was decolorized 90.6% by *P. sordida* YK-624 in a medium containing 3% malt extract for 7 days. Manganese peroxidase (MnP) activity was detected during decolorization by the fungus. By methylation with H_2SO_4 and methanol, linoleic acid methyl ester was also detected from the mycelium. The dye was treated with MnP purified from *P. sordida* YK-624. The dye was decolored by MnP system in the presence of Mn^{2+} and Tween 80. These results suggest that *P. sordida* YK-624 and MnP have potential applications for the cleanup of textile mill effluents.

2001-218

Production and purification of laccase from white rot fungus *Lentites* sp. NP21

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Abstract: The laccase was produced by the thermotolerant wood rotting fungus isolated from tropical rain forest in northern Thailand, *Lenzites* sp. NP21, on solid state fermentation containing the rubber wood chips as a nutrient source. The laccase production was 2.94 units/gram substrate. Addition of 4% (w/v) peptone solution increased the enzyme production yield up to 5.69 units/gram substrate and addition of 150 □M of $CuSO_4$ increased the enzyme produced to 9.43 units/gram substrate. The laccase was purified to the homogeneity using the DEAE-cellulose column chromatography, ultrafiltration and gel filtration on Sephadex G-100 column. The enzyme was purified 893 folds with 49.8% of recovery yield. The optimal pH of enzyme was found at pH 4.0 and the maximum stability, after incubation for 24 hours at various pH, was found from pH 3.5-5.0. The enzyme showed the thermal stability up to 45ºC and decreased continuously at the higher temperature. The half-life of heat inactivation at 55ºC and 60ºC were 130 and 70 min, respectively. The enzyme was inactivated completely with 1 mM Hg^{+2} ion. Further research on characterization of the purified laccase is in progress.

2001-219

白色腐朽菌 *Phanerochaete sordida* YK−624 株の産生するペルオキシダーゼによるリグニンモデル化合物の分解

杉浦むつみ、平井浩文、西田友昭
静岡大学農学部

Degradation of lignin model compound by peroxidase produced by white-rot fungus *Phanerochaete* sordida YK-624

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Faculty of Agriculture, Shizuoka University

Abstract: The peroxidase which involves in the degradation of nonphenolic β-O-4 lignin model compound by white-rot fungus Ph*anerochaete sordida* YK-624 was purified to homogeneity by Mono Q and Superdex 75 chromatographies. The peroxidase was monomeric heme protein, and the molecular weight was about 50 kDa. The study of degradation of nonphenolic β-O-4 lignin model compound by the peroxidase showed that the Cα-Cβcleavage dominantly occurs, and that very small amount of degradation products, which are originated from α-oxidation, β-O-4 bond cleavage and B-ring cleavage, are detected. These oxidative degradation of nonphenolic model were obtained by lignin peroxidase (LiP) from *P. chrysosporium*, however,

more effective degradation was observed with the peroxidase of *P. sordida* YK-624 compared with the LiP.

2001-220

非フェノール性リグニンβ-aryl ether結合の特異的開裂活性を持つ糸状菌の新規細胞外分泌酵素の検出とその分解機能の解析

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Detetiion and isolation of new fungus that cleave the β-aryl ether linkage of high molecular lignin by using the high sensitive assay system

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Abstract: Cleavage of the arylglycerol-β-aryl eher linkage is the most important process in the biological degradation of lignin. The bacterial β-etheras was already described and was tightly associated with the cellular membrane. This function is not able to cleave β-aryl ether linkage in the high molecule lignin, because this enzyme does not secret to extracellular space. In our previous study, the fungal β-aryl ether cleavage enzyme was also described and required the *p*-hydroxyl group and Ca alcohol structure. In this study, we tried the search of the fungi that cleave the β-aryl ethler linkage of non-phenolic structure by extracellular function. We succeeded to isolation the fungus, 2T6-6-strain that has β-aryl ether cleavage function for non-phnolic lignin model compounds.

2001-221

耐塩性白色腐朽菌に関する研究（IV）耐塩性白色腐朽菌 MG-60 株による MnP 産生の海塩添加による促進効果について

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九州大学大学院生物資源環境科学研究科

Study on hypersaline-tolerant white-rot-fungi, (IV). A study on the stimulation of sea salts on MnP production by the salt-tolerant white rot fungus *Phlebia* sp. MG-60

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Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University

Abstract: A white rot marine isolate, *Phlebia* sp. MG-60, secreted manganese peroxidase (MnP) under different sea salt incubation conditions, and its MnP production was strongly enhanced by the added sea salts into incubation media. In this paper, we demonstrate how and why sea salts enhanced the MnP production by *Phlebia* sp. MG-60, and the results pointed out that the combination of NaCl and Ca^{2+} enhanced MnP production as strongly as sea salts.

2001-222

選択的白色腐朽菌 *Ceriporiopsis subvermispora* の菌体外フリーラジカル反応 —NDA による水酸化ラジカル生成反応の抑制

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京都大学木質科学研究所

Extracellular free radical reactions of selective white-rot fungus, *Ceriporiopsis subvermispora*
—Suppression of hydroxyl radical generation by NDA

Hiroko Teranishi, Makiko Enoki, Yoichi Honda, Takashi Watanabe, Masaaki Kuwahara

Wood Research Institute, Kyoto University

Abstract: A selective lignin-degrading fungus, *Ceriporiopsis subvermispora* is able to decompose lignin without morphorogical changes of wood cell walls. Since lignolytic enzymes are too big to penetrate inside of plant cell walls, this fungus decomposes lignin at a site far from enzymes using low molecular mass metabolites. In the wood decaying process, it is expected that the fungus suppresses hydroxyl radical generation to prevent depolymerization of cellulose. In this paper, we report that hydroxyl radical generation by Fenton reaction is suppressed by a novel metabolite of *C. subvermispora*, 1-nonadecene-2, 3-dicarboxylic acid (NDA).

2001-223

ラッカーゼ-メデイエーター系によるポリエチレンとナイロンの分解

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Degradation of polyethylene and nylon in laccase-mediator system
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Faculty of Agriculture, Shizuoka University

Abstract: We investigated whether the laccase-mediator system (LMS) with 1-hydroxybenzo- triazole (HBT) as a mediator could degrade high-molecular-weight polyethylene and nylon-66 membranes. The LMS markedly reduced the elongation and tensile strength of these membranes. After 3 days of treatment with the LMS, the Mw of polyethylene decreased from 242,000 to 28,300, and that of nylon-66 Mw from 79,300 to 14,700. The LMS also decreased the polydispersity (Mw/Mn) of polyethylene and nylon-66. Furthermore, these reductions in elongation, tensile strength, and molecular weight were accompanied by morphological disintegration of the polyethylene and nylon-66 membranes. These results strongly suggest that the LMS with HBT can effectively degrade polyethylene and nylon-66.

2001-224

クラフトパルプ ECF 漂白排水中のダイオキシン類発生レベル

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Dioxins level of kraft pulp ECF bleaching mill sewers
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Abstract: In accordance with the new legislation on dioxin abatement put into effect in Japan in January 2000, kraft and sulfite pulp bleaching mills with chlorine and chlorinated compounds are specified as dioxin generation sources, and since then such pulp mills are subject to restriction of this code. With this code, the concentration of dioxins and coplanar PCBs are restricted below 1 $\text{pg-TEQ}^{\text{WHO1998}}$/L for the river water and below 10pg-TEQ/L for the effluents from the mills. Under the circumstances above, the Hokuetsu Paper Niigata mill converted in April 2000 its conventional bleaching line with the annual production of 200,000 ADMT into an ECF process following the new ECF bleaching line with the annual production of 400,000 ADMT started up in 1998.

2001-225

ダイオキシン分解微生物の新規アツセイ基質によるスクリーニング

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Screening of dioxin degrading microorganisms by new assay substrate
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Abstract: A new method to facilitate rapid and sensitive screening of dioxin degrading microorganisms was developed. The dioxin-like substrates were synthesized with the conjugation of chlorobenzene and fluorescence substrates. Microorganisms including fungi and bacteria are cultivated in liquid culture containing these dioxin-like substrates. Fluorescence based on the cleavage of the dioxin ring of the dioxin-like substrates was measured. The method is especially useful for screening for powerful dioxin degrading strains in natural environments. It eliminates the need for special equipments and laborious analysis which are used for the radiolabeled dioxin. In this study, the new assay method has been used to screen our stock fungi.

2001-226

数種のダイオキシン分解菌を用いた PCB 分解の試み

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愛媛大学農学部

Biodegradation of polychlorinated biphenyls by some microorganisms having ability for degradation of dioxins
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Abstract: To obtain the basic information for purification of polychlorinated biphenyl (PCBs) by bioremediation, microbial degradation of PCB was conducted. Microbial degradation of two kinds of PCBs,

4-chlorobiphenyl (4CB) and 3,3',4,4'-tetrachlorobiphenyl (TCB) was conducted by the three microorganisms, two white-rot fungi (PL1 and 267) and a bacteria screened from the nature,
respectively, in a liquid medium. The two fungi degraded about 90% and 70% of 4CB and TCB, respectively, for 30 days. On the contrary, the bacteria degraded about 20% of TCB were degraded by manganese peroxidase (MnP) and mediator complex system for 24 hours.

2001-227

白色腐朽菌 *Phlebia lindtneri* による dibenzo-*p*-dioxin および dibenzofuran の分解

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Degradation of dibenzo-*p*-dioxin and dibenzofuran by the white-rot fungus, *Phlebia lindtneri*

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Faculty of Agriculture, Kyushu University

Abstract: Dibenzo-*p*-dionxin (DD) and dibenzofuran (DF) was rapidly degraded in lignolytic cultures of the white-rot fungus *Phlebia lindtneri.* Although DF was oxidized to 2- and other position hydroxylated dibenzofuran, the amounts of these metabolites were too little (< 1 %). 2-hydroxy- dibenzofuran (2-OH-DF) was rapidly decreased over 50 times than DD and DF. Significant inhibition of DD and DF degradation was observed in incubation with the cytochrome P-450 inhibitor 1-amino- benzotriazole. In this fact, we concluded that DD and DF were oxidized to hydroxy derivatives by the cytochrome P450, and hydroxy derivatives will be degraded by the further oxidation by the extracellular laccase and /or peroxidase.

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2002-101

単離過程におけるリグニン構造の変化とその要因について

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Stereo preferential degradation of β-O-4 structure during the process of MWL isolation
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Abstract: Beech (*Fagus crenata* Blume) wood meal was milled for 40 to 120 hr with/without toluene by vibratory ball mill to prepare the milled woods, from which the MWLs were isolated by Björkman's method. The derived milled wood and MWL samples were subjected to the ozonation to investigate the changes in E/T ratio and the content of β-O-4 structure. As the milling effect proceeds, both the E/T ratio and β-O-4 content of the milled wood decreased suggesting that the *erythro* β-O-4 structures is more frequently degraded than the *threo* one during the milling. This indicates that the stereo preferential degradation of lignin proceeds during milling. On the other hand, E/T ratio of MWL increased with the progress of milling but was always lower than that of milled wood from which MWL was extracted. MWL seems to be extracted easily from a region with low E/T ratio arid, with the progress of milling, lignins in regions with higher E/T ratio gradually become extractable.

2002-102

MWL 抽出残渣から得た水溶性多糖類に含まれるリグニンの構造

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Structure of small lignin fragment retained in water soluble polysaccharide extracted from MWL isolation residue
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Abstract: Water soluble polysaccharide (WS) was extracted from finely divided softwood residues after extraction of MWL. WS contains only 5.3% of lignin. In a gel filtration curve of WS, lignin was found together with sugars at higher molecular weight part. After treatment of WS with carbohydrate degrading enzyme, the apparent molecular weight of both lignin and sugars decreased significantly. Contrary to this, mild alkaline treatment of WS resulted in the significant decrease of the apparent molecular weight of lignin while that of sugars were almost unchanged. These results may indicate that lignin in WS is present as small fragments attached to polysaccharide chain.

2002-103

MWL 抽出残達への TIZ 法適用の試み

廣澤修一、高野俊幸、中坪文明
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Attempts to application of TIZ degradation method to wood meal after extraction of MWL
Shuichi Hirosawa, Toshiyuki Takano, Fumiaki Nakatsubo
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Abstract: Tosylation of wood meal after extraction of MWL (WMEM) was investigated for TIZ degradation analysis. The degree of tosylation was evaluated by FT-IR. The WMEM was tosylated under conventional TsCl / Pyridine condition, but only small amount of Tosyl group was introduced into the WMEM. Then, the WMEM was divided into three fractions, Cellulose-Lignin fraction (CL),
Hemicellulose-Lignin fraction (HCL), Insoluble-Lignin fraction (IL). Each fraction was highly tosylated under appropriate reaction conditions. Thus, TIZ degradation method may be applied to elucidate total lignin structure in wood.

2002-104

リグニンの β-O-4 結合の生成に対するコンピュータシミュレーション

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Computer simulation on the formation of β-O-4 linkage of lignin

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Abstract: Dehydrogenative polymerization of monolignols was computer-simulated with semi- empirical molecular orbital calculation, MOPAC2002. The reactivity was predicted by activation enthalpy at the transition state with the assumption of a kinetic control. In radical coupling stage, it was predicted that the production ratio of β-O-4 coupling was low compared with those of β-β, β-□ and 5-5 couplings, however, it was increased in non-polar solvent. In the reaction of water to α-carbon of β-O-4 quinonemethide, it was predicted that *threo* form was predominant. However, the reactivity depended on the charge of hydroxyl group and the molecular size of nucleophile.

2002-105

熱分解—TMS 化によるリグニンの分析：けい皮アルコール末端基分析への応用

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Pyrolysis-trimethylsilylation of lignin: a sensitive and easy method for analysis of cinnamyl alcohol-end groups

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Abstract: Pyrolysis in the presence of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA), pyrolysis-trimethylsilylation, was proposed as a new method for analysis of cinnamyl alcohol-end groups in lignin. It preferentially provided large levels of trimethylsilyl (TMS) derivatized cinnamyl alcohols such as coniferyl alcohol diTMS ether (**1**). This method was sensitive to the formed cinnamyl alcohols compared to the conventional pyrolysis and pyrolysis-methylation methods. Pyrolysis-trimethylsilylation of a diazomethane-methylated Japanese cedar (*Cryptomeria japonica*) wood gave two coniferyl alcohol TMS ethers, **1** in 1.3% yield stemming from coniferyl alcohol-end groups and **3** (OMe instead of the phenolic TMS ether of **1**) stemming from the guaiacylglycerol moieties involved in β-O-4 subunits. The results indicated that pyrolysis-trimethylsilylation conveniently provides information on cinnamyl alcohol-end groups when applied to diazomethane- methylated lignins.

2002-106

電子スピン共鳴法によるリグニンの活性酸素消去機能の評価

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生物ラジカル研究所

Evaluation of the active oxygen scavenging activity of lignin using an electron spin resonance method

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Abstract: The superoxide scavenging activity of water solution of lignin extracted from *Quercus acutissima* (KLW) and rice bran (RLW) was evaluated by employing an electron spin resonance cpmbined with the superoxide dismutase addition method. It was found that both samples had superoxide scavenging activity (LLW = 600Unit/g, RLW = 1000Unit/g) with small inhibition rate for superoxide generation in hypoxanthin-xanthine oxidase system (less than 26%).

2002-107

湖沼堆積物のリグニン由来物質

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Lignin-derived matters in surface sediments of Japanese lakes

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Abstract: Lignin derived matters were detected by degradative methods chemically from the surface sediments of three kinds of lake, Biwa, Seto-Taisho and Fukami, located in Japan. Monomers of lignin fragments obtained by CuO oxidation and thioacidolysis were quantified by GC. Dimers obtained by desulphulation of thioacidolysis products were analyzed by GC-MS. In all samples, biphenyl (5-5') structures were dominant among the dimerer compounds derived from lignin.

2002-108

維管束および木繊維における多糖—リグニン結合の定性的・定量的考察

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Covalent associations between lignin and polysaccharides in vascular bundle and fiber of plant

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Asian Natural Environmental Science Center, the University of Tokyo

Abstract: In this study, structural evidences of each type of cell wall were discussed on the view-point of covalent associations between lignin and polysaccharides, which were evaluated qualitatively and quantitatively with carboxymethylation followed by water extraction for vascular bundle, fiber and compound middle lamella separated from some plants. Chemical composition of vascular bundles and fibers, and secondary walls and compound middle lamella of plants and structural feature of Björknan lignin isolated from their walls were also investigated. Role of covalent associations between lignin and polysaccharides in different types of cell walls was discussed for subsistence and effective utilization of plants on the basis of these results.

2002-109

ペルオキシダーゼ／H_2O_2によるモノリグノール類酸化速度に対する 3，5 位置換基の影響

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The effect of 3,5-substituents on oxidation rates of monolignols by peroxidase/H_2O_2 as oxidant

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Abstract: It is thought that one-electron oxidation of Monolignols is mainly catalyzed by peroxidase/H_2O_2 in lignification in the cell wall. To elucidate the process of lignification in the all wall, it is important to clarify the mechanism of one-oxidation of monolignol by peroxidase/H_2O_2. In this study, to investigate the difference of the reactivity of monolignols in terns of 3,5-substituents, the order listed as to oxidation rates of monolignols and 3,5-subsdtuted monolignols with Horseradish Peroxidase (HRP) /H_2O_2 as oxidant and the order listed as to oxidation potential of them, which were measured with cyclic voltammetry, were compared.

2002-110

白色腐朽菌 *Phanerochaete sordida* YK−624 株の産生するペルオキシダーゼについて(II)

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静岡大学農学部

Peroxidases produced by white-rot fungus *Phanerochaete sordida* YK−624 **(II)**

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Abstract: The hhhitor for peroxidases produced by *Phanerochaete sordida* YK−624 was investigated. The inhibitor, of which the molecular weight was less than 10 kDa, was purified by gel permeation chromatography. The inhibitor inhibited the oxidation of verahyl alcohol (VA) by YK-PO1, YK-PO2 and lignin peroxidase, although the inhibitor did not affect on he reactions of manganese peroxidase and horseradish peroxidase (HRP). In the spectral analysis, compound I of YK-PO2 changed to the native state of YK-PO2 by the addition of the inhibitor, although compound I of HRP did to compound II. On the other hand, little change of compound I of YK-PO2 to native state was observed by the addition of the inhibitor. The inhibitor inhibited VA oxidation by YK-PO1 in an uncompetitive manner.

2002-111

リグニンペルオキシダーゼの酸化反応機構：電気化学的特性からの考察

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Redox mechanism of lignin peroxidase: Electrochemical characterization

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Abstract: Electrochemical analysis of lignin peroxidase (LiP) was performed using a pyrolytic graphite electrode coated with peroxidase-embedded tributylmethyl phosphonium chloride membrane. The formal redox potential for the ferric/ferrous couples of LiP was found to be -126 mV (vs. SHE), which was comparable with that of manganese peroxidase and horseradish peroxidase p*Ka* values for the distal His in peroxidases were calculated using the Nernst equation, to be 5.8 for LiP, 4.7 for MnP, and 3.8 for HRP. A high p*Ka* value of the distal His might be crucial for LiP compound II to uptake a proton from the solvent. Therefore, LiP is able to complete its catalytic cycle during the oxidation non-proton-donating substrates with a low pH optimum.

2002-112

白色腐朽菌 *Pleurotus ostreatus* により生産される MnP アイソザイムの発現調節について

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The analysis of expression on the production of manganese peroxidase by white-rot fungi *Pleurotus ostreatus*

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Wood Research Institute, Kyoto University, Akita Prefectural University

Abstract: Manganese peroxidase (MnP) was secreted by *Pleurotus ostreatus* in liquid stationary culture. Two different MnP isozymes were produced in glucose/Yeast-extract medium (GY) and peptone/glucose/yeast-extract medium (PGY). The isoelectric points of MnP produced in GY medium (MnP-GY) and PGY medium (MnP-PGY) were found to be 3.70 and 3.95, respectively. The molecular masses of both isozymes were 42 kDa. N-terminal amino acid sequences of MnP-PGY was found to be identical to that of MnP 3. It was also similar to that of MnP which was produced in the sawdust culture. To better understand a MnP isozyme production system for medium content, RT-PCR analysis was performed.

2002-113

カワラタケの遺伝子導入系の確立

仁田由美[*1*2]、（森総研）宮崎安将[*3]、中村雅哉[*3]、飯村洋介[*4]、
宍戸和夫[*5]、（農工大院 BASE）梶田真也[*2]、諸星紀幸[*2]
[*1] 株式会社コシダテック、[*2] 農工大院 BASE、[*3] 森林総合研究所、[*4] 産業技術総合研究所、[*5] 東京工業大学生命工学科

Development of transformation system in *Coriolus versicolor*

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Abstract: Since white rot fungi have a system for the degradation of lignin and various types of persistent organic polutants (POPs), it has been proposed that these fungi are useful for bioremediationand bioconversion of them. A white-rot basidiomycete, *Coriolus versicolor*, secrete laccase abd the enzyme contribute to degrade lignin and POPs. In this study, we tried to establish the transformation system in order to over-produce gene of enzyme such as laccase in *C. versicolor.* We constracted pT7GPDHPT vector containing promotor of glyceraldehydes-3-phosphate dehydrogenase (gpd) gene from *C. versicolor* with hygromycin B resistance gene as marker gene. This plasmid vector was integrated into genome of *C. versicolor* ard resultant transformations could be selected on medium including hygromycin B.

2002-114

メソ多孔体による酵素の超安定化と無塩素パルプ漂白への応用

杉山英彦, 梶野勉, 高橋治雄
株式会社豊田中央研究所

Enzyme stabilization in mesoporous material and its application for TCF pulp bleaching

Hidehiko Sugiyama, Tsutomu Kajino, Haruo Takahashi
Toyota Central R & D Laboratories, Inc.

Abstract: Enzymes were adsorbed on the silica mesoporous materials and their stabilities were studied. Both the surface character and size matching between pore sizes and the molecular diameters of enzyme were important in achieving a high stability. Manganese peroxidase (MnP) immobilized in mesoporous material,

whose pore size just matched the diameter of the enzyme, showed the best stability and high H_2O_2 tolerance. We constructed a thermally discontinuous two stage reactor system (TSRS), in which the enzyme and pulp bleaching reactions were separately performed. After treatment of pulp with TSRS, the brightness of pulp increased to about 85% within 6hr.

2002-115
特別講演：
非水媒体中における酸化還元酵素の機能発現とその応用
後藤雅宏
九州大学大学院工学研究院、科技団さきがけ 21
Invited Lecture: Catalytic activatiom of peroxidase in nonaqueous media and its novel application
Masahiro Goto
Department of Applied Chemistry, Kyushu University

Abstract: Activatiion of peroxidase in an organic solvent by reversed micell or surfactant coating method was investigated. Lyophilized LIP from an optimized aqueous solution exhibited no enzymatic activity in any organic solvents examined in his study; however, LIP was catalytically active by being entrapped in the AOT reversed micellar solution. LIP activity in the reversed micelle was enhanced by optimizing either preparation or oparation conditions such as water and pH in water pools of the reversed micelle, and the raction temperature. The degradation reaction of several environmental pollutants was attempted using LP hosted in the reversed micelle.

2002-116
特別講演:
リグニンの加溶媒分解 —ホモリシス、クレゾリシス、アルドソリシス、アセトソリシス
佐野嘉拓
北海道大学大学院農学研究科
Invited Lecture: Solvolysis of lignin, - Homolysis, cresolysis, acetosolysis and aldosolysis
Yoshihiro Sano
Graduate School of Agriculture, Hokkaido University

Abstract: Depolymerization and solubilization of lignin by solvolysis are of primary importance for industrial processes of wood proceeded by heating at different pH such as pulping processes as well as for fundamental lignin chemistry. We have been studying the mild hydrolysis of lignin with 50% aqueous dioxane at 180ºC for 20 min for the chemical structure of lignin, and solvent pulping processes, solvolysis pulping with 50% aqueous cresol, atmospheric AcOH pulping with a small amount of mineral acid and HBS pulping with aqueous high-boiling alcoholic solvent for the fractionation of lignocelluloses. Also the reaction mechanisms for their processes have been studied using lignin model compounds. This paper reviews the reaction mechanisms of lignin by solvolysis processes in hot neutral, weakly acidic and weakly alkaline solutions.

2002-201
酸加水分解リグニンの陰イオン交換樹脂への変換
松下泰幸、安田征市
名古屋大学大学院生命農学研究科
Preparation of anion-exchange resins from acid hydrolysis lignin
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Graduate School of Bioagricultural Sciences, Nagoya University. Nagoya

Abstract: One of the key points in developing saccharification process is to find effective ways to utilize acid lignin. The authors investigated the chemical conversion into anion-exchange resins of phenolized acid lignin (P-SAL), prepared from acid lignin by phenolation with sulfuric acid catalyst, by two methods. The restricted resinification of P-SAL followed by Mannich reaction to yield a weakly basic anion-exchange resin with 2.4 meq/g ion exchange capacity. Another method is the reaction of resinified P-SAL with glycidyltrimethylammonium chloride to yield a strongly basic anion-exchange resin with 2.1 meq/g ion exchange capacity.

2002-202
リグニン系ポリウレタン複合材料の力学物性に及ぼす充填材形状の影響

船橋正弘[*1]、廣瀬重雄[*1]、畠山立子[*2]、畠山兵衛[*3]
[*1] 産業技術総合研究所、[*2] 大妻女大学家政学部、[*3] 福井工業大学工学部

Effect of filter shape on mechanical properties of lignin-based polyurethane composites

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[*1]National Institute of Advanced Industrial Science and Technology, [*2]Otsuma Women's University,
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Abstract: Polyurethane (PU) composites were prepared using a lignin polyol (KLP, a mixture of kraft lignin and polyethylene glycol, Mw=200) diphenylmethane diisocyanate (MDI) and fillers. Wood meal and coffee grounds were used as fillers. The mixture of KLP and fillers was reacted with MDI by adding an adequate amount of acetone as a solvent. Mechanical properties of composite samples were determined by compression tests. Master curves of the relationships between the specific values of mechanical properties and the apparent volume ratio, determined as the ratio of the apparent volume of filters to the reciprocal values of the apparent density of the samples, were obtained.

2002-203

リグノスルフォン酸ソーダのナノレベル構造と熱的性質

畠山兵衛[*1]、角野浩崇[*1]、善定和博[*1] 畠山立子[*2]
[*1] 福井工業大学工学部、[*2] 大妻女大学家政学部

Nanoscale morphology and thermal properties of sodium lignosulfonate

Hyoe Hatakeyama[*1], T. Sumino[*1], Kazuhiro Zenjyo[*1], Tatsuko Hatakeyama[*2]
[*1]Fukui University of Technology, [*2]Otsuma Women's University

Abstract: Sodium lignosulfonate (NaLS) has been examined using differential scanning calorimetry (DSC) and tapping mode atomic force microscopy (AFM). NaLS from aqueous solutions was deposited onto freshly cleaved mica surfaces and then air-dried. AFM images of NaLS showed clear network structure at the concentration of 10 pg/ml. DSC was carried out at the scanning rate of 10ºC/min from -150ºC to 200ºC. Glass transition was observed for a dry sample. However, glass transition, cold crystallization and melting of water were observed for wet samples.

2002-204

非塩素系漂白過程における α-カルボニル型リグニン構造の挙動（III）: パルプ残存リグニン中の α-カルボニル型リグニン構造の挙動

友田生織、松本雄二、飯塚堯介
東京大学大学院農学生命科学研究科

Formation and degradation of α-carbonyl structure in lignin during chlorine free bleaching, (III)
Formation and degradation of α-carbonyl structure in lignin remaining in pulp

Iori Tomoda, Yuji Matsumoto, Gyosuke Meshitsuka
Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: We have already proposed a new method to evaluate the content of α-carbonyl structure in residual lignin without isolating the lignin from the pulp. In this report, we applied this method to MWL and soft wood oxygen-bleached kraft pulp (NOKP) , and the changes in the content of α-carbonyl structure during alkali and alkali hydrogen peroxide treatment were evaluated. In MWL experiment, hydrogen peroxide treatment under pH13 was very effective to reduce the α-carbonyl content, but pH10 was not as effective as pH13. The results of hydrogen peroxide treatment of NOKP suggested that hydrogen peroxide bleaching is a process in which the formation and degradation of α-carbonyl structure take place at the same time.

2002-205

広葉樹クラフトパルプのオゾン・過酸化水素を用いる無塩素漂白

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筑波大学農林工学系

Non-chlorine bleaching of hardwood kraft pup with ozone and hydrogen peroxide

Tsutomu Ikeda, Hiroshi Ohi
Institute of Agricultural and Forest Engineering, University of Tsukuba

Acid treatment was developed for non-chlorine bleaching with ozone and hydrogen peroxide. Medium consistency ozone bleaching of hard wood oxygen delignified kraft pup required higher ozone charge than high consistency ozone bleaching did to bleach al a given brightness. Although, high consistency ozone bleaching could not keep a viscosity at an acceptable level, medium consistency ozone bleaching could keep it. Hexeneuronic acid could be removed by both acid treatment and ozone bleaching. Then, a bleaching sequence with acid treatment and ozone bleaching could decrease the ozone charge and improve bleaching selectivity.

2002-206

酸性条件下におけるリグニンの反応機構：アシドリシス条件下におけるリグニン構造の変質に関する分析

坂口智一、松本雄二、飯塚堯介
東京大学大学院農学生命科学研究科

Rcaction mechanism of lignin under acidic conditions. Analysis of structural modification of lignin during acidolysis

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Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Acidolysis by the use of hydrochloric acid has been widely applied to the analysis of chemical structure of lignin (analytical acidolysis), and to the isolation of lignin (preparative acidolysis). Compared with analytical acidolysis, preparative acidolysis employs milder condition. It is considered that preparative acidolysis gives less chemical changes of lignin than analytical acidolysis. In this work, wood meal and milled wood lignin (MWL) were treated under several acidolysis conditions and structural modification caused by acid treatment was quantitatively analyzed by ozonation method. Not only the solubilized part but also the solid part (precipitates for MWL and residual lignin for wood meal) were analyzed.

2002-207

Kinetic and mechanism of the degradation of non-phenolic lignin model compounds under aerobic polyoxometalate (POM) bleaching conditions

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[*1] Department of Wood and Paper Science, North Carolina State University, [*2] USDA Forest Service, Forest Products Laboratory

Abstract: A non-phenolic lignin model compound, ***1***, ***2*** and ***4***, was reacted with polyoxometalate (POM) under anaerobic bleaching conditions, and the kinetic and mechanism were investigated. A syringyl type, ***1***, was degraded slower than a guaiacy1 type, ***2***, although the activation energy of ***1*** is a little lower than ***2***. Instead, the frequency factor of ***1*** is considerably smaller than ***2***, suggesting that steric factor controls the rate of the reaction between POM and model compound, and dominates over electronic property of its aromatic ring. The significance of steric factor was confirmed by the reaction using ***4*** that has an ethoxyl group instead of a methoxyl group. The degradation of ***4*** was slower than ***1***, giving a lower activation energy and a much smaller frequency factor. A kinetic isotope effect was observed when the α-deuterated compound of ***1*** and 2 was subjected to the reaction. It is suggested that the rate-determining step of the reaction between POM and non-phenolic models is the Abstraction of the benzylic hydrogen. Further kinetic and mechanism will be discussed in the presentation.

2002-208

Structural characteristics of lignin in humified materials

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Abstract: The behavior of lignocellulosic material during humification was investigated using grass compost. Lignin of grass compost prepared by the Björkman's method suggested that lignin macromolecules were modified even after short time composting. Soluble fraction of composted grasses gave the same products with lignin by alkaline nitrobenzene oxidation and by ozonation, and also by methoxyl group determination. These results suggested that some portion of lignin macromolecules were biologically modified to be dissolved in water by introduction of hydrophilic groups such as carboxyl groups, which could play same role as soil humic matters.

2002-209

β-O-4 型側鎖の立体構造を規定する要因の解明 --樹種間における β-O-4 型側鎖立体構造の分布--

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Distribution of diastereomeric forms of β-O-4 structures among different wood species

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Abstract: The *erythro/thero* ratios of β-O-4 structures were investigated by the ozonation analysis for about 20 species including both softwood and hardwood. The *erythro/threo* ratio exhibited wide variation among species, about 1.0 for softwood and 1.5-3.5 for hardwood. The correlation between *erythro/thero* ratios of β-O-4 structures and the methoxyl group contents were clearly observed among the species. lt was confirmed that there is the relationship between the *erythro/thero* ratio and syringyl/guaiacyl ratio among different species, suggesting that the aromatic ring type is one of the factors which control the formation of diastereomeric forms of β-O-4 structures during lignin biosynthesis.

2002-210

熱帯モンスーン気候と温帯における樹木主要成分の生分解過程の定量的・定性的考察

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Qualitative and quantitative discussions for biodegradation of wood components in the tropical monsoon area and in the temperate area

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Abstract: Urban green spaces should be promoted in tropical monsoon area such as in the Philippines, where their effects on mitigation of urban climate would be expected to be greater than those in temperate area. Huge amounts of plant residues produced under high plant productivity should be utilized as resources. This study discusses the process of biodegradation of plant remains into soil organic matter for their utilization. Quantitative and qualitative analyses were carried out to discuss changes in biomass weight, lignin weight (Klason lignin and acid soluble lignin), aromatic composition of lignin and neutral sugar composition of major urban trees in the Philippines during biodegradation. The results were compared with those carried out in Japan.

2002-211

落葉のマルチング過程におけるリグニン量の変化

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Changes in lignin content of leaf litters during mulching

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Abstract: Alkaline nitrobenzene oxidation procedure, ozonation method and methoxyl content determination have been applied to the decomposing leaf litters during mulching to investigate the properties of lignin and to approximately estimate lignin content as assumed lignin content during mulching. Assumed lignin content based on methoxyl content of Klason residue was much lower (3.9 to 10.0%) than that of Klason residue (37.1 to 46.7%). Absolute amount of assumed lignin somewhat decreased during mulching, while the structure of lignin remaining in leaf litters alter mulching was not quite different from its original structure.

2002-212

ケイヒ酸／モノリグノール経路のメタボローム解析に用いる重水素標識モノリグノールの合成

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Syntheses of deuterium-labelled monolignols for metabolome analysis of the cinnamate/monolignol pathway

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Abstract: In the postgenomic era, much attention has been focused on the overall understanding of the

metabolism of the cinnamate/monolignol pathway in relation to lignin, lignan and norlignan biosynthesis. Recently, transcriptome and proteome analysis of the pathway has been reported. On the other hand, metabolome analysis has not been yet applied to the pathway, because of the lack of an appropriate methodology. Herein, we have synthesized deuterium-labelled monolignols, which can be used for internal standards of stable isotope dilution method-guided metabolome analysis of the cinnamate/monolignol pathway.

2002-213

新生木部におけるリグニン前駆物質配糖体の挙動

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名古屋大学大学院生命農学研究科

On the behaviors of gluasides of lignin precursors in the differentiating xylem

Yukiko Tsuji, Seiichi Yasuda and Kazuhiko Fukushima

Graduate School of Bioagricultural Sciences, Nagoya University

Abstract: To clarify the mechanism of storage and supply of monoligno1 in the metabolism of lignin, the roles and behaviors of coniferin and coniferyl aldehyde glucoside in lignin biosynthesis were examined by tracer experiments using labeled precursors. The microautoradiography showed coniferyl aldehyde glucoside was incorporated into lignin with almost similar pattern to the case of coniferin. The results of lignin chemical analysis, DFRC/GC-MS ensured that coniferyl aldehyde glucoside was metabolized as monolignol precursor. Coniferin might be incorporated into lignin through the complex pathway with oxidative step that is independent of coniferin/β-glucosidase system.

2002-214

イネをモデルとした植物細胞壁形成過程に関する研究（1）—イネ科植物細胞壁成分の生合成制御に関する研究—

間瀬浩平[*1]、佐藤かんな[*1]、中野仁美[*1]、西窪伸之[*1]、北野英己[*2]、梶田真也[*1]、片山義博[*1]

[*1] 東京農工大学大学院生物システム応用科学研究科、[*2] 名古屋大学大学院生命農学研究科

Studies on genetic regulation of cell wall formation in rice plant (1) —The research on biosynthesis control of cell wall component in the Gramineae plant

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[*1]Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, [*2]Graduate school of Bioagricultural Sciences, Nagoya University

Abstract: It is obvious that genes involved in lignin biosynthesis have to be coordinately regulated in response to developmental and environmental cues. So, we think that the elucidation of regulation mechanisms of such genes is effective for the acquisition of useful characteristics such as environmental adaptation and blocking of the ingress of pathogens and increase in the biomass resource. The rice plant in which genome analysis advances is very useful in order to understand these regulation mechanisms using the genetic and molecularbiological technique. In this study, as a part of program characterizing the biosynthetic regulation of plant cell wall component, we examined the polysaccharide-linked hydroxycinnamoyl esters biosynthetic pathway and its molecular mechanism of genetic regulation in rice plant using rice one gene recessive mutant.

2002-215

イネをモデルとした植物細胞壁形成過程に関する研究（2）—イネ細胞壁成分の生合成制御遺伝子のマップベースクローニングと新しい2次壁形成異常を持つイネの解析—

佐藤かんな[*1]、間瀬浩平[*1]、北野英己[*2]、梶田真也[*1]、片山義博[*1]

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Studies on genetic regulation of cell wall formation in rice plant, (2) —Map based cloning of biosynthesis control gene of cell wall component and analysis of novel secondary cell wall mutant

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Abstract: The plant cell walls are composed of a complex mixture of phenolic component, carbohydrates and proteins. To date, the structure and biosynthesis of major cell wall components, lignin and cellulose have been clarified, but the co-ordinate regulations of individual steps in end biosynthetic pathway and different pathways through cell wall establishment remain unclear. To understand these co-ordinate regulations, we perform map based cloning of *d50* gene which induces abnormal parenchyma cell walls in Fukei71 as shown in previous presentation. In addition, using histochemical and cheical methods, we analyze a novel rice mutant of alterations in the thick secondary cell wall formation.

2002-216
白色腐朽菌のバイオレメディエーション環境下でのモニタリング
須原弘登[*1]、大黒千映子[*1]、近藤隆一郎[*2]
[*1] 九州大学大学院生物資源環境科学研究科、[*2] 九州大学大学院農学研究院
Monitoring of white-rot fungus during bioremediation
Hiroto Suhara, Chieko Daikoku, Ryuichiro Kondo
Faculty of Agriculture, Kyushu University

Abstract: Bioremediation is a low-cost treatment alternative for the cleanup of dioxin- contaminated environment, when pollution spread broad-ranging. An interesting fungus was isolated from white rotten wood of a broadleaf tree from Kyushu island, in Japan, named strain MZ-340. This isoiate has ability to degrade dioxin. We have tried to use this strain for bioremediation of dioxin- contaminated environment *on site*. Hence, we have to develop a PCR-based assay to detect strain MZ-340 reliably on bioremediation site. We successfully monitored the strain MZ-340 *on site*. The relationship between the population of the fungus and the effect of bioremediation by this fungus will be discussed.

2002-217
ペルオキシダーゼ及び遷移金属反応を開始系とするリピッドペルオキシデーションによる加硫・未加硫イソプレンゴムの分解
佐藤　伸[*1]、本田与一[*1]、渡辺隆司[*1]、桑原正章[*2]
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Degradation of vulcanized and non-vulcanized isoprene rubbers by lipid peroxidation initiated with peroxidases and transition metals
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[*1]Wood Research Institute, Kyoto University, [*2]Institute of Wood Technology, Akita Prefectural University

Abstract: Degradation of vulcanized and non-vulcanized synthetic polyisoprene (IR) by lipid peroxidation initiated with peroxidases and transition metals was analyzed by $CHCl_3$-extraction,

gel permeation chromatography. and double-shot pyrolysis GC-MS (DS-Py-GCMS). Non- vulcanized IR was depolymerized intensively by the free radicals from unsaturated fatty acids produced by manganese peroxidase (MnP), Mn(III) chelate, and the Fenton reagent (FR). Partial depolymerization was observed in lipid peroxidation with horseradish peroxidase (HRP) and laccase/mediator. Distinct degradation was not observed in the reactions with lipoxygenase (LOX). In these reaction systems, the depolymerization of polyisoprene depended on the presence of peroxidizable lipids. Degradation of vulcanized IR sheets was observed in the lipid peroxidation initiated by FR. Reactions by MnP and Mn(III) chelate in sodium oxalate buffer also degraded the rubbers. The reaction system by FR degraded the vulcanized rubber sheet intensively as 80 % of the rubber component was solubilized with $CHCl_3$. By the DS-Py-GCMS analysis of $CHCl_3$ extracts, low molecular mass fragments, isoprene, 1,4-dimethyl-4-vinylcyclohexene, 1-methyl-5-(1-methyl- ethenyl)-cyclohexene and limonene were identified. These results indicate that control of free radical chain reactions of lipids by enzymes and transition metals is a key to degrade the recalcitrant vulcanized rubber products.

2002-218
リグニン分解酵素による Irgarol の分解
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Degradation of Irgarol by ligninolytic enzymes
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Abstract: 2-Methylthio-4-*tert*-butylamino-6-cyclopropylamino-*s*-triazine (Irgarol 1051), which is a newly developed herbicidal additive for use in copper-based antifouling paints, was treated with partially purified MnP and laccase. The HPLC data showed that lrgarol 1051 disappears by 36-37% after a 24-h treatment with both enzymes and two peaks suspected the transformation products of Irgarol 1051 are newly formed by the treatment. One of the transformation products was identified to be

2-methylthio-4-*tert*-butylamino-6-amino-*s*-triaxine (M1) by comparing its retention time and mass spectrum with those of an authentic compound using GC-MS. This suggests that *N*-dealkylation occurs at the cyclopropylamino group of Irgarol 1051 resulting in metabolite M1. Toxicities of Irgarol 1051 and M1 were evaluated by the growth inhibition tests using alga (*Selenastrum capricornutum*) and duckweeds (*Lemna gibba* and *L. minor*). M1 showed the toxicity about 10 times lower than that of Irgarol 1051 for all the aquatic plant species tested, indicating that the treatment with ligninolytic enzyme is effective in detoxification of Irgarol 1051.

2002-219

木材腐朽担子菌による Polych1orinated Naphthalenes の分解

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Degradation of poychlorinated naphthalenes by wood decaying fungi

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Abstract: The transformation of polychlorinated naphthalenes (PCNs) has been studied using six strains of wood decaying fungi. In one of these strains, *Phlebia lindtneri* GB-1027degraded 2-chloronaphthalene (2CN) immediately. The initial metabolites were detected by gas chromatography-mass spectrometry. The hydroxylation of substrates was initially observed during degradation of 2CN. Significant inhibition of degradation of 2CN was observed in incubation with cytochrome P-450 monooxygenase inhibitors, 1-aminobenzotriazole and piperonyl butoxide. These experiments with cytochrome P-450 monooxygenase inhibitors, and formation of the mono- hydroxylated metabolites suggested that *P. lindtneri* initially degraded 2CN by monooxygenases oxidation system.

2002-220

白色腐朽菌 *Phlebia lindtneri* による塩素化 dibenzo-*p*-dioxin および dibenzofuran の酸化

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Oxidation of chlorinated dibenzo-*p*-doxin and dibenzofuran by white-rot fungus; *Phlebia lindtneri*

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Abstract: The actions of white-rot fungus on two chlorinated aromatic compounds, known to be persistent environmental contaminants, were studied. Two both-ring chlorinated dioxin-models, 2,7-dichlorodibenzo-*p*-doxin (2,7-diCDD) and 2,8-dichlorodibenzouran (2,8-diCDF), were metabolized by white-rot fungus *Phlebia lindtneri*. 2,7-DiCDD was disappeared linearly in he culture of *P. lindtneri*, after a 20 day incubation period, only 45 % remained in die culture. One of metabolites each produced by *P. lindtneri* from a 5-day incubated culture with 2,7-diCDD or 2,8-diCDF was identified by gas chromatography-mass spectrometry. *P. lindtneri* was shown to metabolize 2,7-diCDD and 2,8-diCDF to a hydroxy-diCDD and a hydroxy diCDF, respectively.

2002-P01

微生物相互作用による白色腐朽菌の酵素生産

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Induction of ligninolytic enzyme production in white-rot fungi by antagonistic microorganisms

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Abstract: We investigated enzyme production in white-rot fungi by antagonistic microorganisms. Fungi often produce the phenoloxidase enzyme laccase during interactions with other organisms. By pairings of white-rot fungi *Trametes versicolor* or *Lentinus edodes*, and antagonistic organism *Trichoderma longibrachiatum* on malt extract agar, laccase activity was mainly detected on the region in contact with both fungi. On the other hands, manganese peroxidase (MnP) activity was detected on the region in contact with *T. longibrachiatum* in the case of white-rot fungus *Phanerochaete sordida*.

2002-P02

白色腐朽菌 *Phanerochaete sordida* YK−624 株の産生するペルオキシダーゼについて(III）

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Peroxidases produced by white-rot fungus *Phanerochaete sordida* YK-624 (III)
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Abstract: The characteristics of two peroxidase isozymes (YK-PO1, YK-PO2), produced by *Phanerochaete sordida* YK-624 were investigated. The substrate specificities of lignin peroxidase from *P. chrysosporium* (Pc-LiP), YK-PO1, and YK-PO2 for monomeric lignin model compounds were not differ. On the other hand, dimeric β-O-4 lignin model compound was more efficiently consumed by YK-POl and YK-PO2 than by Pc-LiP. Moreover, YK-PO1 had a higher specificity for sinapyl alcohol oligomer than did YK-PO2 and Pc-LiP, though the specific activity of veratryl alcohol (VA) oxidation was the lowest with YK-PO1. YK-PO1 showed high tolerance to hydrogen peroxide compared with YK-PO2 and Pc-LiP. It is thought that low reactability of YK-PO1 with hydrogen peroxide affects on VA oxidation by YK-PO1.

2002-P03

非フエノール性 β-*O*-4 型リグニンモデル化合物の酸化電位とラッカーゼ／1−HBT 系による酸化力との相関

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The correlation between the oxidation potentials of non-phenolic β-*O*-4 lignin model compounds and the oxidation abilities of laccase/1-HBT system
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Abstract: We have studied on the degradation of non-phenolic β-*O*-4 lignin model compounds by laccase/1-HBT system. In this Study, we investigated the oxidation potentials and HOMO energies of non-phenolic β-*O*-4 lignin model compounds (1)-(7). These results suggest that the oxidation ability of laccase/1-HBT system correlates with their oxidation potentials and HOMO energies.

2002-P04

スジチヤダイゴケ（*Cyathus stercoreus*）による非フエノール性リグニンモデル化合物の分解とリグニン分解酵素

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Dqadadon of non-phenolic lignin model compound by *Cyathus stercoreus* and its lignin degrading enzymes
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Abstract: The white rot fungus *Cyathus stercoreus* degraded a non-phenolic β-*O*-4 lignin model compound, 1,3-dihyroxy-2-(2,6-dimethoxyphenoxy)-1-(4-ethoxy-3-methoxyphenyl) propane [I] , in Tien and Kirk medium. The fungus catalyzed the β-ether cleavage and the aromatic ring cleavage of substrate I. Furthermore, the enzyme activities of extracellular fluid of *C. stercoreus* were investigated_

2002-P05

白色腐朽菌によるダイオキシン汚染土壌のバイオレメディエーションにおける土壌成分の影響

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Effect of soil components on bioremediation of dioxin-polluted soil by white-rot fungi
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Abstract: A white-rot fungus, *Ceriporia* sp. MZ-340 is able to degrade polychlorinated dibenzo-*p*- dioxins and polychlorinated dibenzofurans. However, dioxins in soils are hardly degraded by the fungus. In order to clarify inhibitory effect of soil components on the degradation of dioxins by the fungus, glass beads and soil were used as carriers for dioxins. As model compounds for dioxins, 2,7-dichlorodibenzo-*p*-dioxin (DCDD) or octachlorodibenzo-*p*-dioxin (OCDD) were added to the glass beads or soil, and treated with the fungus.

Although both DCDD and OCDD added on glass beads were degraded extensively, the degradation of both DCDD and OCDD added on soil was inhibited completely. Furthermore, toluene extracts of soil was suggested to affect inhibitively on the degradation of DCDD.

2002-P06

Polych1orinated Biphenyls (PCBs)の酵素による分解の試み

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Biodegradation of polychlorinated biphenyl by enzymes from fungus having ability for degradation of dioxins

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Abstract: To obtain the basic information for purification of polychlorinated biphenyls (PCBs) by bioremediation, degradation of PCBs by crude enzymes from fungus PL1 having ability for degradation of dioxins was tried in this research. Two kind of PCBs, 4-Chlorobiphenyl (4CB) and 3,3',4,4'-Tetrachlorobiphenyl (TCB) were used as substrates. About 74% and 13% of 4CB and TCB were degraded by the crude enzymes from fungus PL1 in a liquid medium for 24 hours, respectively. And furthermore, about 33% and 26% of 4CB and TCB in a soils were degraded by the crude enzymes from fungus PL1 for 30 days, respectively. From the results obtained here, it was found that PCBs could be degraded by crude enzymes from fungus having ability for degradation of dioxins.

2002-P07

白色腐朽菌ミノタケが分泌する新規リグニンペルオキシダーゼの触媒特性

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Characterization of novel lignin peroxidase from the white-rot basidiomysete *Trametes cervina*

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Abstract: Among several white-rot basidiomycetes examined, *Trametes cervina* was found to show relatively higher lignin peroxidase (LiP) activity in the extracellular medium. Utilizing DEAE Sepharoe FF, Sephadex G-100, and Mono Q, LiP from T. *cervina* (TcLiP) was purified. TcLiP was obtained as a major band with Mr of 37 kDa but with a minor band on SDS-PAGE analysis. Further study revealed that the minor band was derived from a contamination of MnP. However, the contamination was minimal; thus, steady-state kinetic and spectroscopic analyses could be achieved. Electron absorption spectrum of TcLiP shows a typical characteristics for a hexa- coordinate high spin ferric iron state of the heme.

2002-P08

担子菌の示す細胞応答機構の解析：外因性有機化合物が引き起こす種々の応答反応

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Fungal cellular responses against exogenous chemicals

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Abstract: Extracellular ligninolytic enzymes are thought to be involved in the initial attack on polymeric lignin and aromatic pollutants via the one-electron oxidation mechanism, resulting in the formation of a variety of aromatic and quinoid fragments which are further metabolized intracellularly. Therefore, basidiomycetes seem to have highly regulated and specific intracellular metabolic systems for each fragment. However, a fungal cellular response mechanism against chemical compounds has not been well studied. In this study, the fungal responses occurred against the addition of a wide variety of chemicals to fungal cells were analyzed using transcriptomic, proteomic, and metabolomic techniques.

2002-P09

8-O-4’型シリンギルネオリグナンのジアステレマーの立体化学とトチュウにおけるそれらの生合成

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Stereochemistry of 8-*O*-4' syringyl neolignans and their biosynthesis in *Eucommia ulmoides*

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Abstract: 8-*O*-4' type neolignans, syringylglycerol-8-*O*-4'-(sinapyl alcohol) ether (SGSE) and guaiacylglycerol-8-*O*-4'-(sinapyl alcohol) ether (GGSE) were synthesized. Their *erythro* and *threo* isomers were separated and identified by means of NMR. To understand their biosynthesis in *Eucommia ulmoides,* feeding experiments of a labeled precursor, [8-^{14}C]sinapyl alcohol, to excised shoots were undertaken. It was found that the radioactivity was incorporated into SGSE (and its glucoside) in the stems and the leaves, and that the present incorporation into *erythro* isomer was more than that into *threo* isomer.

2002-P10

クラフトパルプの漂白過程で生成する高分子成分の生分解挙動

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Biodegrdation of high-molecular-weight compounds produced by kraft pulp bleaching process

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Biodegradation behavior of high molecular portion of kraft pulp bleach effluent containing substantial amount of organochlorine was investigated. Chlorine-based bleach liquor containing microorganisms was subjected to dialysis cultivation to trace low-molecular –weight degradation products (MW<1000), some of which may cause environmental impact. A few degradation products were successively detected as intermediary metabolites by HPLC equipped with UV detector (270nm).

It was observed that abou 50 % of organically bound chlorine in the fraction was removed during the incubation period of three months.

2002-P11

ケナフ靭皮の中間温度での蒸解

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Pulping or kenaf bast fiber at moderate temperature

Faculty of Agriculture, Kochi University

Abstract: It was already shown that it is possible to make a high viscosity kenaf bast pulp by normal pressure soda pulping although the residual lignin is still at high level. To realize a commercial pulping to make high viscosity (strength) pulp, it is needed to reduce the lignin content and the lord of bleaching even if some reduction of viscosity occur. A moderate temperature pulping was examined here to reduce the residual lignin content of unbleached pulp. At 140ºC, the pretreatment of ammonium oxalate was not effective to the delignification, but viscosity was kept comparatively at high level. The addition of anthraquinone and the extension of keeping time at 140ºC was proved to be effective. The viscosity was 62 cp and the Kappa number was 39.

2002-P12

シラカンバ常圧酢酸パルプの無塩素漂白（2）

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Non-chlorine bleaching of atmospheric acetic acid pulp from *Betula platyphylla var. japonica* Hara, (2)

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Abstrct:Atmospheric acetic acid pulp from Japanese white birch wood was treated with non-chlorine bleaching agents such as oxygen (O), ozone (Z) and chlorine dioxide (D). In the previous investigation we showed that the pulp was fully bleached with multi-stage bleaching in DEDED or ZZZEpD sequence. In order to decrease the amount of ozone or chlorine dioxide, oxygen bleaching was performed in this investigation. Deacetylation of

the pulp prior to oxygen bleaching was essential. Bleachability of the pulp was improved by EO treatments, and brightness reached 86-87% ISO in EOZED sequence. However, paper strength of the pulp was inferior to that in DEDED or ZZZEpD sequence. Further investigations were necessary to optimize oxygen bleaching stage.

2002-P13

HBS パルプ化におけるリグニンの構造変化 —NMR による解析（2）—

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Structural changes in lignin during HBS pulping. -NMR Analysis, (2)

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Abstract: Structural changes in lignin during HBS pulping were investigated by quantitative ^{13}C-NMR and HMQC spectra. The content of phenolic hydroxyl groups in MWL increased significantly, which nay be attributed to hydrolysis of α-*O*-4 bonds and homolytic cleavage of phenolic β-aryl ether. The decrease in the content of β-*O*-4 structures and introduction of 1,4-butanediol into α-position of β-*O*-4 moiety were confirmed. The β-5 and β–β substructures were relatively resistant to HBS pulping conditions, but β-1 may not. The signals corresponding to Hibbert's ketones were not observed, which suggests that acidolysis is not important degradation pathway in HBS pulping.

2002-P14

アルカリ性酸素脱リグニン段排液リグニンの土壌改良剤としての性状

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Characterization of lignin fragments in alkaline-oxygen stage waste liquor as soil conditioning agent

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2002-P15

酸可溶性リグニンのクロロホルム可溶成分

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Chloroform soluble components of acid soluble lignin

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Abstract: To elucidate the formation and chemical structures of chloroform soluble materials in acid soluble lignin (ASL), lignin model compounds of arylglycero1-β-aryl ethers with guaiacyl (I) and syringyl (II) nuclei were treated by the KIason procedure. Model compound I gave only insoluble polymerized condensation product, while II gave insoluble polymerized product and chloroform soluble low molecular weight products, which were dissolved in 3% sulfuric acid.

2002-P16

リグニンと新聞古紙を原料とする成形活性炭ボードの作成

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Preparation of activated carbon boards from a mixture of lignin and waste newspaper

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Abstract: Activated carbon boards (ACB) were prepared from mixture of hardwood acetic acid lignin (HAL) and waste newspaper. The mixture was molded to precursory boards by thermal press, and then converted to ACB by carbonization and steam activation. The ACB prepared from the precursory boards with 20% HAL molded under the conditions of 130ºC and 6 MPa showed the most excellent adsorption properties and flexural strength among the ACB tested. The adsorption ability and flexural strength of ACB were deteriorated with the increase in the board thickness. The laminated ACB with 3 layers showed better adsorption property than that of mono layer ACB with the corresponding thickness.

2002-P17

リグニンの構造および反応研究のための ^{13}C-標識 NMR 示差スペクトル分析法

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Carbon 13-NMR spectrometry measuring difference between spectra of ^{13}C- enriched and unenriched lignins. —An effective tool for analysis of structure and reactions

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Abstract: Lignin is a structurally heterogeneous polymer formed by an irreversible random polymerization of several kinds of monolignol radicals. Therefore, it is impossible to degrade ligninquantitatively into monomeric or oligomeric units, and degradation loses information on heterogeneity. Accordingly, destructive analyses can provide limited information on the chemical structure of lignin macromolecule. Nondestructive analyses by ^{13}C-NMR difference spectrometry between spectra of specifically ^{13}C-enriched lignin and unenriched lignin can provide definite information not only on the structure of lignin macromolecule but also on the structural change during various reactions that is hardly obtained by any other conventional destructive analyses. Information on the structural heterogeneity can also be obtained by combination of this technique with pulse labeling and anatomical separation techniques.

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2003-101

TOF-SIMSによるリグニン構造の解析

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Analysis of lignin structures by TOF-SIMS
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Abstract: Lignin model compounds were investigated using time-of-flight secondary ion mass spectrometry (TOF-SIMS) to study the relationship between the chemical structure and the secondary ion spectra. The formation mechanism of two prominent fragment ions (m/z 137 and 151), each of which has a CG-CI Structure With a guaiacyl nuclei, was deduced by using deuterium labeling of specific positions of coniferyl alcohol. We also examined 8-O-4', 8-1', 5-5', 8-5' and 8-8' types of dimers, showing dominant C_6-C_1 ions originated from specific inter-unit bonds in lignin.

2003-102

近赤外分光計測による植物葉リグニンの定量

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Estimation of lignin content in fallen leaves using near-infra-red spectroscopy
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Abstract: It is important to develop the measuring method of organic matter in conjunction with carbon circulation or global warming. Near-infra-red (NIR) spectroscopy may be an effective method to estimate contents of organic matter such as lignin. Lignin contents of fallen leaves were determined using various analytical procedures. In laboratory, NIR spectra were recorded for each sample of leaves on ground. The correlation coefficient between NIR spectra and lignin content varied with analytical procedures used to determine lignin content and plant species. The combination of plant species and analytical method should be considered to develop a suitable regression model using NIR spectroscopy.

2003-103

光による熱帯産材の変色とそれらのスペクトルの特徴

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[*1] 北海道立林産試験場、[*2] 島根大学総合理工学部
Photo-induced color changes of some tropical woods and their spectral features
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[*1]Hokkaido Forest Products Research Institute, [*2] Interdisciplinary Faculty of Science and Engineering, Shimane University

Abstract: Although for bangkirai (*Shorea* spp.), jahhra (*Eucalyptus marginata*) and robusta (*E. robusta*), both □a* (shify to red) and □b* (yellowing) decreased with increased exposure time up to 600 h, for auri (*Acacia auriculiformis*), cumaru (*Amnurana acreana*), ipe-high (*Tabebuia* spp. with relative high speciflc gravity), ipe-low (with relative low specific gravity), keruing (*Dipterocarpus* spp.), □b* increased with exposure up to 50 h, and decreased above 50 h. Further information on the
correlation between the above color changes and their spectral features such as diffuse reflectance Fourier transform infrared (DRIFT) and ultraviolet-visible (UV-Vis.) spectra are given at the presentation.

2003-104

マカンバMWL抽出残渣から得た水溶性多糖類に含まれるリグニンの構造

相見 光、松本雄二、飯塚堯介
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Structure of small lignin fragment retained in water soluble polysaccharide extracted from birch MWL isolation residue

Hikaru Aimi, Yuji Matsumoto, Gyosuke Meshitsuka
Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: To investigate the structural feature of lignin existing nearby the lignin-carbohydrate linkages, water soluble fraction with low lignin content was prepared from the residual Birch wood meal after the extraction of MWL. Gel filtration behavior before and after treatment with polysaccharide degrading enzyme revealed that this fraction was composed of relatively high molecular weight polysaccharide to which small lignin fragments were linked. Structural analysis of lignin in this fraction revealed that it is rich in syringyl nuclei with non-condensed type structures and have different character in condensed type one.

2003-105

アシドリシス条件下におけるリグニン構造の変質に関する分析（2）

坂口智一、松本雄二、飯塚堯介
東京大学大学院農学生命科学研究科

Analysis of structural modification of lignin during acidolysis (2)

Tomokazu Sakaguchi, Yuji Matsumoto, Gyosuke Meshitsuka
Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: In the last lignin symposium, we reported that about 25% of β-O-4 structure was lost under preparative acidolysis condition (0.1M HCl in dioxane-water, reflux for 2h), and that α-condensed structure was not detected even under 5% sulfuric acid treatment by ozonation analysis. In this work, Hibbert's ketone type side-chain structure of acidolysis MWL was quantitatively analysed by $NaBH_4$ reduction followed by ozonation. In this result, it was indicated that about 45% of β-O-4 structure was lost during analytical acidolysis (0.2M HC1, reflux for 4h) and about 40% of lost β-O-4 structure was converted into C6-C3 type Hibbert's ketone structure. However, C6-C3 type Hibbert's ketone structure was not detected when H_2SO_4 was used as catalyst.

2003-106

花弁道管部におけるトラケアリー・エレメントの形成とリグニンの化学構造

勝亦京子[*1]、飯山賢治[*1]、江前敏晴[*2]
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Genesis of tracheary element and chemical structure of lignin at vessel of flower petal

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[*1]Asian Natural Environmental Science Center, the University of Tokyo, [*2]Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: It is hardly recognized the presence of lignin in flower pedals. But frower pedals have to be supplied water through vessels, which may be quite different from "normal vessels" in other tissues of plant. Vessels of flower pedals are characterized by quick formation and significantly short life span. The vessels would be excellent specimens to investigate the formation of secondary walls in plants. Morphology of vessels of flower pedals of 14 popular species were observed by light and scanning electron microscopies, and found tracheary element structures from all of specimens. In addition, chemical composition of secondary walls of camellia (*Camellia reticulata* Lindl.) was analyzed and structural feature of Björkman lignin isolated from camellia was investigated. Lignin was significantly rich in p-hydroxyphenyl nuclei and condensed structure, which could characterize as initial stage of lignin biosynthesis.

2003-107

樹木の防御反応としてのリグニン生合成について

堀啓映子[*1]、谷田貝光克[*1]、山田利博[*2]
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Lignin biosynthesis for defense responses against fungus

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[*1]Graduate School of Agricultural and Life Sciences, the University of Tokyo, [*2]Experimental Station at Tanashi, University Forests, the University of Tokyo

Abstract: Mass mortality of oaks is caused by the infection of a fungus *Raffaelea quercivora*, vectored by ambrosia beetle *Platipus quercivorus*. Reaction zone barrier (RZB) was observed near the discolored part in the infected wood. Lignin content of RZB was higher than the other part, and S/V ratio was lower. Guaiacyl type and condensed type lignin was synthesized for the defense response against fungus in the reaction zone barrier.

2003-108

イネをモデルとした植物細胞壁形成過程に関する研究（3）−イネ科植物細胞壁成分の生合成制御に関する研究−

中野仁美[*1]、間瀬浩平[*1]、佐藤かんな[*1]、北野英己[*2]、梶田真也[*1]、片山義博[*1]
[*1] 東京農工大学大学院生物システム応用科学研究科、[*2] 名古屋大学大学院生命農学研究科

Studies for genetic regulation of cell wall formation in rice plant (3)- The research on biosynthesis control of cell wall component in the Gramineae plant

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[*1]Graduate School of Bio-Applications and System Engineering, Tokyo University of Agriculture and Technology, [*2]Graduate School of Bioagricultural Sciences, Nagoya University

Abstract: The series of genes involved in the biosynthesis of lignin and polysaccharide-linked hydroxycinnamoyl esters, which compose plant cell walls, have to be coordinately regulated in order to respond and adapt to environmental stresses during plant growth process. The rice plant that genome analysis make advance is very useful in understanding these regulation mechanisms using the genetic and molecular biological technique. In this study, as a part of program characterizing the biosynthetic regulation of plant cell wall component, we examined the polysaccharide-linked hydroxycinnamoyl esters biosynthetic pathway and its molecular mechanism of genetic regulation in rice plant with rice one gene recessive mutant.

2003-109

ラッカーゼ反応系における 1-Hydroxybenzotriazole の役割

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[*1] 静岡大学農学部，[*2] 京都府立大学大学院農学研究科

The role of 1-hydroxybenzotriazole in laccase reaction system

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Abstract: We investigated the role of 1-hydroxybenzotriazole (HBT) in laccase (Lac) reaction system. No metabolites which were produced from a non-phenolic β-O-4 lignin model compound in Lac/HBT system was detected in artificial HBT radical system, although the artificial HBT radical degraded the model compound. In the kinetics studies, HBT was not a competitive inhibitor for Lac, and the inhibition pattern was changed by the addition of HBT. On the other hand, HBT was an uncompetitive inhibitor for horseradish peroxidase (HRP). Moreover, ferrocytochrome c was competitively oxidized by Lac/HBT system. These results suggest that HBT might be involved in the formation of ES complex, but not a radical mediator.

2003-110

ポプラ分化中木部におけるラッカーゼの局在

竹内美由紀、高部圭司、藤田　稔
京都大学大学院農学研究科

Localization of laccase in differentiating xylem of poplar

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Graduate School of Agriculture, Kyoto University

Abstract: Laccases and peroxidases are thought to be the candidates for dehydrogenative polymerization of monolignols, however their differences have not been clarified. We have, therefore, investigated the localization of these two enzymes in poplar trees using immunocytochemistry to reveal the possible difference between laccases and peroxidases in their localization and perhaps the role in lignification. For immunolabeling of laccase, antibodies were raised against the peptides synthesized according to the amino acid sequences of laccase. The labeling of laccase was observed in the cell walls of secondary wall forming fibers and vessels, especially in compound middle lamella and in outer layer of secondary wall. In parenchyma cells, intensive labeling was seen in the innermost layer of cell wall.

2003-111

リグニン生合成の抑制による飼料消化性の向上

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Down regulation of cinnamoyl-CoA reductase(CCR) induces increase of cell wall digestibility in rice (*Oryza*

sativa)

Kentaro Kubo, Shinya Kawai

Faculty of Agriculture, Tokyo University of Agriculture &Technology

Abstract: Cinnamoyl-CoA reductase(CCR) is the first enzyme to the lignin-specific biosynthesis. Inverted repeats constructs of the DNA encoding CCR of *Oryza sativa* have been introduced into rice plants. Some CCR down-regulated plants displayed phenotype like *Brownn midrib* mutants. Histochemical analysis was performed on the transformants. The internodes from them, in contrast to wild type, indicated weaker red staining when treated with phloroglucinol-HCl. This suggested reduction in aldehydes and/or lignin contents. Little difference was detected between wild type and transformants with the Mäule reagent.

2003-112

超高感度蛍光アツセイシステムにより見出されたリグニンのβ−aryl ether結合を特異的に切断する糸状菌の分解機能とその多様性

大塚祐一郎[*1]、中村雅哉[*2]、菱山正二郎[*2]、梶田信也[*1]、片山義博[*1]

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Detection, characterization and its diversity of new fungus that cleave the β-aryl ether linkage of high molecular lignin by using the high sensitive assay system

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[*1]Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, [*2]Forestry and Forest Products Research Institute

Abstract: Cleavage of the arylglycerol-β-aryl ether linkage is the most important process in the biological degradation of lignin. The bacterial β-etherase was already described and was tightly associated with the cellular membrane. This function is not able to clave β-aryl ether linkage in the high molecule lignin, because this enzyme does not secret to exbacellular space. In this time, we aimed to detect and isolate of the fungi catalyzing cleavage of β-aryl ether linkage of high molecular lignin in the soil fungi. We screened and isolated the several fungi, named 2BW-1, f5053,2T6-6,FA1 and FC5 by using GOU, GOUbz and DHP-GOU as the high sensitive assay system. Resulting

analysis of 18srDNA, we determined that these fungi belong to Ascomycetes and it suggest that various fungi affect to degrade the phenolic compounds of plant involving lignin in nature.

2003-113

リグナン生合成の系統分類的多様性

梅澤俊明

京都大学木質科学研究所

Phylogenetic aspects of lignan biosynthesis

Toshiaki Umezawa

Wood Research Institute, Kyoto University

Abstract: The chemical structures of lignans vary substantially in basic carbon frameworks, as do their oxidation levels and substitution patterns. In this review, the phylogenetic distribution of plants producing 66 typical lignans with a variety of chemical structures are listed based on a data base search. The distribution is correlated with the possible biosynthetic pathways of the lignans and discussed from evolutionary aspects.

2003-114

アベマキ及びイチョウ外樹皮におけるスベリン芳香族部分の予想前駆体と外樹皮のメタノリシス分解生成物の比較

鈴木利貞、滝野修平、泉 大輔、片山健至

香川大学農学部

Predicted precursors of the aromatic domain of suberin and methanolysis products of two kinds of outer bark: comparison between *Quercus variabilis* and *Ginkgo biloba*

Toshisada Suzuki, Shuhei Takino, Daisuke Izumi, Takeshi Katayama

Faculty of Agriculture, Kagawa University

Abstract: *p*-Hydroxycinnamic acid esters, as predicted precursors of the aromatic domain of suberin, in two kinds of bark of *Quercus variabilis* and *Ginkgo biloba* were analyzed. The esters were specifically present in both of the outer bark. Dehydrogenative polymerizations of butyl ferulate and butyl caffeate were carried out as a model system. The polymerization of butyl ferulate gave dimers of β-O-4’, β-5', dihydronaphthalene,

naphthalene and β-β’symmetry types. The polymerization of butyl caffeate afforded dimers of β-6' and dihydronaphtharene types. Extractive free powders obtained from the two kinds of bark were treated by methanolysis. Feruloyloxy fatty acid esters and methyl ferulate were isolated from both of the decomposition products.

2003-115
特別講演:
樹木心材成分の生理活性と生成
坂井克己
九州大学大学院生物資源環境科学研究科
Invited Lecture: Bioactivity and production of heartwood components
Kokki Sakai
Faculty of Agriculture, Kyushu University

Abstract: Here I review our works on anti-tyrosinase activity of the *Artocarpus incisus* heartwood and steroid 5α-reductase inhibitory of resveratrol oligomers isolated from Shorea spp. heartwood. Contribution of the 2,4-dihydroxyphenyl structure to the anti-tyrosinase activity is noted. Dehydrogenative polymerization of resveratrol yielded 5α-reductase inhibitory oligomers. ln addition, I deal with our studies on hinokitiol (β-thujaplicin), a heartwood constituent of Cupressaceae species exhibiting a variety of bioactivities. Its production by *Cupressus lusitanica* cell cultures, signal transduction after elicitation, and biosynthetic pathway has been studied.

2003-116
特別講演:
自然に学ぶ高分子合成の現状
蒲池幹治
福井工業大学工学部
Invited Lecture: Development in nature-inspired polymer synthesis
Mikiharu Kamachi
Fukui University of Technology

Abstract: Molecular design in polymer synthesis has been inspired by fine functions of natural polymers. Remarkable advance has been made in artificial control of molecular weight in chain- growth polymerization, preparation a helical polymers, application of enzymes to polymer synthesis, and matrix polymerization due to supra molecules. In this lecture, living radical polymerization, asymmetric polymerization, enzymatic polymerization, and preparation of tubular polymer from cyclodextrin are mentioned.

2003-201
□-*O*-4 結合からなる規則性人工リグニンポリマーの化学合成
岸本崇生、浦木康光、生方　信
北海道大学大学院農学研究科
Synthetic lignin polymer composed of β-*O*-4 structure
Takao Kishimoto, Yasumitsu Uraki, Makoto Ubukata
Graduate School of Agriculture, Hokkaido University

Abstract: The β-*O*-4 structure is one of the most important substructures in lignin. In this investigation, highly regulated synthetic lignin polymers composed of β-*O*-4 structure were prepared from simple aromatic compounds as starting materials by a solution polymerization method. Acetophenone derivatives were brominated and polymerized in the presence of K_2CO_3. The polymer was converted to synthetic lignin polymer composed of β-*O*-4 structure. The polymer was soluble in usual lignin solvents such as 1,4-dioxane and DMSO. Molecular weight of acetate derivatives of the polymer was determined by GPC analysis.

2003-202
β-*O*-4 型リグニンオリゴマーの簡便な合成法の検討
片平　類、上高原浩、高野俊幸、中坪文明
京都大学大学院農学研究科
Facile synthetic method for β-*O*-4 type lignin oligomers
Rui Katahira, Hiroshi Kamitakahara, Toshiyuki Takano, Fumiaki Nakatsubo

Graduate School of Agriculture, Kyoto University

Abstract: A novel synthetic method for obtaining lignin oligomers that are composed of only the β-*O*-4 structure was investigated. This method consists of two reaction steps: the continuous nucleophilic addtion oligomerization of butoxycarbonylmethyl vanillin (**1**) and subsequent reduction of the oligomeric β-hydroxyl ester. In the first step, the oligomeric β-hydroxyl ester (**2**) was obtained in 90% yield; the repeating units of these oligomers were joined exclusively by β-*O*-4 linkages. The number-average degree of polymerization of **2** was calculated to be about 7.2 (Mw/Mn=1.36). In the second step, the oligomeric β-hydroxyl ester (**2**) was treated with $LiAlH_4$ to give product **3** in 73% yield. On the basis of NMR, MALDI-TOP-MS, and GPC analysis of the acetate of **3**, it was indicated that compound **3** is an oligomeric lignin related compound containing only β-*O*-4 interunit linkage.

2003-203
熱帯泥炭湿地環境中有機物の性状と土壌有機物形成過程

金　貞福、勝亦京子、飯山賢治
東京大学アジア生物資源環境研究センター

Chemical characterization of peat organic materials

Zhenfu JIN, S. Kyoko Katsumata, Kenji Iiyama
Asian Natural Environmental Science Center, the University of Tokyo

Abstract: A series of structural features of the three main humic fractions, namely humic acid, fulvic acid and humin from different depths of peat profile in Narathiwat Province, southern Thailand were isolated and analyzed. Humin and humic acid contained similar amount of total carbon and nitrogen in acid insoluble fractions of humin and humic acid. Ash free acid insoluble fractions in humin ranged from 76.4% to 86.2% of original peat samples and there was no significant difference among different peat profiles. Contents of methoxyl groups and total yield of alkaline nitrobenzene oxidation products were significantly lower than those of fresh wood specimens. Those values increased with depth of sampling and the amount of water extractives, the content of acid soluble lignin and the ratio of acid to aldehyde of alkaline nitrohenzene oxidation products showed the same trend.

2003-204
ケナフ茎芯加溶媒分解物から繊維強化型ポリウレタン

執行　薫[*1]、堀　成人[*1]、竹村彰夫[*1]、小野拡邦[*1]、飯山賢治[*2]
[*1] 東京大学大学院農学生命科学研究科、[*2] 東京大学アジア生物資源環境研究センター

Fiber reinforced polyurethane film prepared from solvolysis product of Kenaf (*Hibiscus cannabinus* L.) core

Kaoru Shigyo[*1], Naruhito Hori[*1], Akio Takemura[*1], Hirokuni Ono[*1], Kenji Iiyama[*2]
[*1]Graduated School of Agricultural and Life Sciences, the University of Tokyo, [*2]Asian Natural Environmental Science Center, the University of Tokyo

Abstract: Solvolysis of Kenaf (*Hibiscus cannabinus* L.) core with polyethylene glycol (PEG) is studied to acquire plant-biomass-derived polyols from which polyurethane products are prepared. Conventional study to obtain alternative oil resources from the biomass has focused on the solubilization as much as possible. In this work, the solvolysis is carried out to the extent of that the cellulose fiber remains in the solvolyzed crude. Polyurethane products prepared from this crude would be reinforced with the residual fiber. This report deals with 1) optimization of solvolysis condition suited to the above idea, 2) mechanical properties of the polyurethane films prepared from the solvolyzed.

2003-205
Development of effective utilization of rice waste−byproducts

Maxima E. Flavier[*1*2], Kyoko S. Katsumata[*1], Kenji Iiyama[*1]
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Development of effective utilization of rice waste-byproducts.

Maxima E. Flavier[*1*2], Kyoko S. Katsumata[*1], Kenji Iiyama[*1]
Asian Natural Environmental Science Center, the University of Tokyo, Institute of Chemistry, University of the Philippines Los Banos

Abstract: This study involved the chemical and structural characterization of 80% aqueous ethanol-extracted samples of rice hull, straw and bran including amylase-treated and roasted bran. Neutral sugar composition, uronic acids, C:N ratio, lignin by acetyl bromide, hydroxycinnamic acids and nitrobenzene

oxidation products were determined.

2003-206

リグニン分解のシステム解析を目指した *Phanerochaete chrysosporium* のゲノム解析

割石博之[*1]、志水元亨[*2]、平塚宣博[*2]、湯田直樹[*2]、松崎芙美子[*2]、廣瀬宣子[*2]、野中大輔[*2]

[*1] 九州大学大学院農学研究院、[*2] 九州大学大学院生物資源環境科学研究科

Functional genomic studies on *Phanerochaete chrysosporium* for systematic determination of lignin degradation mechanisms

Hiroyuki Wariishi, Motoyuki Shimizu, Nobuhiro Hiratsuka, Naoki Yuda, Fumiko Matsuzaki, Noriko Hirose, Daisuke Nonaka

Faculty of Agriculture, Kyushu University

Abstract: To better understand mechanisms involved in fungal ability to degrade lignin and a wide variety of aromatic compounds, systemic analysis on cellular mechanisms is believed to be projected. Functional genomics seems to be a starting point for such studies. In the present study, recent situations for fungal genomic research will be briefly summarized. Furthermore, our recent data on genome annotation of *Phanerochaele chrysosporium* will also be discussed.

2003-207

耐塩性白色腐朽菌 MG-60 株の産生するマンガンペルオキシダーゼの発現特性（2）

大黒千映子[*1]、須原弘登[*2]、堤　祐司[*3]、近藤隆一郎[*3]

[*1] 九州大学大学院生物資源環境科学研究科、[*2] 有明工業高等専門学校、[*3] 九州大学大学院農学研究院

Characterization and expression of manganese peroxidase produced by halotolerant white-rot fungus *Phlebia* sp. Mg-60 (2)

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Abstract: *Phlebia* sp.MG-60 is a ligninolytic basidiomycete isolated from mangrove stands based on its lignin degradative ability. This fungus can grow and exhibit high lignin degrading ability under the culture condition with high salt concentration. In this study, we investigated the production of manganese peroxidase (MnP) by MG-60. When MG-60 was grown in the medium containing 3% sea salts, it showed higher MnP activity than that in the medium without sea salts. MG-60 produced different MnP isoenzymes under the conditions with or without sea salts, and two partial cDNAs encoding MnP isoenzymes were cloned and sequenced. Investigation of the expression of these MnP mRNA levels under different sea salts conditions is now undergoing.

2003-208

白色腐朽菌 *Ceriporiopsis subvermispora* の菌体外代謝物 ceriporic acid B の物理化学的性質

大橋康典、寺西紘子、渡辺崇人、本田与一、渡辺隆司

京都大学木質科学研究所

Physico-chemical properties of ceriporic acid B, an extracellular product by *Ceriporiopsis subvermispora*

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Wood Research Institute, Kyoto University

Abstract: *Ceriporiopsis subvermispora* produces alk(en)yl itaconates (ceriporic acids). In the present study, physico-chemical properties of ceriporic acid B were examined. The acid dissociation constants, pKa_1 and pKa_2 of ceriporic acid B determined in H_2O/EtOH (1:1, v/v) by pH titration were 4.5 and 8.2, lower than those of itaconic acid (3.6 and 5.0). This result suggests that carboxylic structures were stabilized by a long side chain of ceriporic acid B. Ceriporic acid B strongly inhibited reduction of Fe(III) by L-cysteine. The inhibitory effects were suppressed by chelators such as NTA and EGTA. These results suggest that ceriporic acid B coordinates to Fe(III) and decreases reactivity of Fe(III) with the reductant.

2003-209

白色腐朽菌およびその酵素によるポリアクリル酸の分解

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Biodegradation of polyacrylic acid by white rot fungi and ligninolytic enzymes

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Faculty of Agriculture, Shizuoka University

Abstract: Super absorbent polymer (SAP), which is a crosslinked polymer of polyacrylic acid (PAA), was solubilized by treatments with white rot fungi and ligninolytic enzymes, manganese peroxidase (MnP) and laccase (Lac), and water-soluble PAAs were detected as metabolites. White rot fungi also degraded PAA and the decrease of Mw of PAA was enhanced under LN culture without glucose. Furthermore, the degradation of PAA by MnP and Lac was observed. These results suggest that white rot fungi and ligninolytic enzymes can degrade PAA and have potential applications to decrease environmental levels of water-soluble polymers.

2003-210

白色腐朽菌の産生する酵素による塩素化芳香族化合物の脱塩素について

若月亜希子、平井浩文、西田友昭
静岡大学農学部

Dechlorination of polychlorinated aromatic compounds by enzymes from white-rot fungi

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Faculty of Agriculture, Shizuoka University

Abstract: Ligninolytic enzymes from white-rot fungi, manganese peroxidase (MnP), laccase (Lac), and lignin peroxidase (LiP), were used in an attempt to treat methoxychlor (MC), a chemical widely used as a pesticide and an environmental contaminant. MC was converted into methoxychlor olefin (MCO) and 4,4'-dimethoxybenzophenone by MnP or laccase treatment. These results indicate that ligninolytic enzymes from white-rot fungi can catalyze the oxidative dechlorination of MC. The culture fluids from various white-rot fungi decreased 2,4,8-trichlorodibenzofuran (TCDF) by 20-40% after a 24-h treatment. Most of TCDF was dechlorinated and polymerized by the culture fluids. In fact, the dechlorinase was separated with anion-exchange chromatography from the culture fluid inoculated with *P. sordida* YK-624. These results suggest that white-rot fungi secrete hydrolytic dechlorinase, and that the dechlorinase eliminates Cl ion from TCDF and inserts hydroxyl group to TCDF, and that the metabolites which contain hydroxyl group would be oxidized by phenol oxidase, and then polymerized.

2003-211

新規塩素化ダイオキシン分解微生物の分解機能に関する研究（II）

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Screening and functional analysis of chlorinated dibenzo-p-dioxin degrading microorganisms by dioxin-like assay substrate

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Abstract: We developed a fluorometric assay method for rapid and sensitive evaluation of dioxin degrading capacity by microorganisms. The dioxin-like substrates for fluorometric assay of dioxin degrading microorganisms were synthesized with the conjugation of chlorobenzenes and fluorescence substrate. Cleavage of the ether bridge in these assay substrates would yield the highly fluorescent products. *Bacillus midousuji* SB2B-J2 was isolated from the compost in Osaka by professor Hoshina. The isolated bacterium could degrade chlorinated dibenzo-p-dioxins in the fly ash. The capability of this bacterium for dioxin degradation was analyzed by using the dioxin-like assay substrates biochemically. During incubation of the bacterium with the assay substrates, fluorescence based on the cleavage of the dioxin ring was detected. The activity for the cleavage of the ether bridge in dioxin ring was detected in a membrane fraction of cell free extract from *B. midousuji* SH2B-J2.

2003-212

白色腐朽菌によるダイオキシン汚染土壌の処理

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Treatment of polychlorinated dioxin-polluted soil by white-rot fungi

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Abstract: When dioxin-polluted soil was treated by *Ceriporia lacerate* MZ-340, no decrease of dioxin, contents of octachlorodibenzo-*p*-dioxin (OCDD) and octachlorodibenzofuran (OCDF), was observed. However, when dioxin-polluted soil pretreated with HCl was treated by the fungus, the decrease of OCDD and OCDF contents was observed. This result indicated that characteristics of soil components (organic and inorganic state) may affect the degradation activity of the fungus. To establish bioremediation technology to treat dioxin-polluted sludge under sea, 2,7-dichlorodibenzo- *p*-dioxin (2,7-DCDD) was treated by white-rot fungi under hypersaline condition. The halotolerant white-rot fungus, *Phlebia* sp. MG-60 was observed to have an ability to degrade 2,7-DCDD under hypersaline condition.

2003-213

多糖加水分解酵素による MWL 抽出残渣の分解挙動 〜Cellu1ose-Lignin fraction について〜

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The behavior of degradation of wood meal after extraction of the MWL by carbohydrate-degrading enzymes -Analysis of cellulose-lignin fraction

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Abstract: Cellulase and xylanase were used to investigate the structure of Cellulose-Lignin fraction (CL), which was extracted from wood meal after extraction of the MWL with LiCl/ DMAc. The peaks in the elution curves of CL from UV detector, which was derived from lignin containing component, was almost corresponding to the peaks in the curves of CL from RI detector, which was due to all components. In the both enzyme treatments, the behaviors of main peaks from UV detector were similar to that of main peaks from RI detector. They indicated that lignin was connected sugar component.

2003-214

リグニンの熱分解機構 —生成物の高分子化について—

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Polymerization mechanism of lignin during pyrolysis

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Abstract: A series of lignin model compounds were pyrolyzed at 250ºC for 2 h to investigate the polymerization mechanism of lignin. Two types of the mechanisms were suggested to be involved in the polymerization; one is via radical intermediates formed by dehydrogenation of phenolic hydroxyl group and Cα-hydrogen, and the other is via quinone methide-type intermediates. At 250ºC, the latter quinone methide mechanism was dominant and phenolic unit had much higher reactivity than the corresponding non-phenolic one. Furthermore, Cβin vinylguaiacol was found to have higher reactivity than the aromatic ring in their nucleophilic attack to the quinone methide-type of intermediate.

2003-215

熱分解−トリメチルシリル化による広葉樹リグニンの分析

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Analysis of hardwood lignins by pyrolysis-trimethylsilylation

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Abstract: Pyrolysis of softwood lignins in the presence of *N,O*-bis(trimethyl-silyl)trifluoro- acetamide (pyrolysis-trimethylsilylation, BSTFA/Py) provides coniferyl alcohol and aldehyde trimethylsilyl (TMS) ethers stemming from both terminal phenylglycerol moieties and cinnamyl end-groups. To deep the BSTFA/Py chemistry of lignin, this method was applied to hardwood lignins. The results with syringyl dehydrogenative polymers and a tochinoki milled wood lignin showed that BSTFA/Py provides sinapyl alcohol and aldehyde TMS ethers, with high sensitivity. The yield ratios of sinapyl to coniferyl alcohol TMS ethers (SA/CA) were determined with hardwood type lignins. Most of the lignins showed good correlation between the SA/CA ratios and the yield ratios of syringaldehyde to vanillin (S/V) by nitrobenzene oxidation. Kenaf bast and some

hardwood lignins showed rather lower SA/CA ratios than expected from their S/V ratios.

2003-216

シダおよびコケ植物に存在するリグニンの分析的熱分解法による解析

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Characterization of fern (Pteridophytes) and moss (Bryophytes) *in situ* lignins by analytical pyrolysis

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Abstract: Nine ferns and 10 mosses were analyzed by pyrolysis-trimethylsilylation (TMS-Py) and pyrolysis-mass spectrometry (Py-MS). In TMS-Py, coniferyl alcohol derivative (CA) was detected from an ferns samples, and sinapyl alcohol derivative (SA) was detected only from Iwahiba (*Selaginella tamariscina*). Iwahiba, Haiboragoke (*Crepidomanes birmanicum*) and Matsubaran (*Psilotum mudum*) provided the CA peak distinctly. In Py-MS of these ferns, ions derived from lignin were detected. In TMS-Py of mosses, a trace amount of CA was detected from Aohaigoke (*Rhynchostegium riparioides*), Futoryuubigoke (*Hylocomium brevirostre*) and Kumonosugoke (*Pallavicinia longispina*). Oomizugoke provided trace amounts of CA and SA.

2003-217

種々のアルカリ条件下でのパルプ処理における過酸化水素の役割

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The role of hydrogen peroxide during pulp treatment under several alkali conditions

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Abstract: Hydrogen peroxide bleaching is important in non-chlorine bleaching. However, there are many unknown parts in the role of hydrogen peroxide during pulp bleaching. We have shown increase of vanillin yield that was produced by nitrobenzene oxidation, after hydrogen peroxide treatment of oxygen bleached kraft pulp. We applied kappa number method to hydrogen peroxide treated pulps and treatment liquors to analyze lignin and other permanganate consuming compounds. The data show that hydrogen peroxide has at least two different roles. Ionized/non-ionized hydrogen peroxide can remove pulp kappa number. Ionized hydrogen peroxide has another hidden role that is against alkali-promoted creation of permanganate consuming substances.

2003-218

Comparison of different treatment sequences of kenaf bast fiber for high viscosity pulp

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Abstract: This paper explores the production of high viscosity pulp from kenaf bast by using three different treatment sequences (A, B and C). The chemical compositions (cellulose, hemicellulose and lignin contents) and viscosity from these treatments were determined. Yield and kappa number of sample B are the highest one, while sample A shows the highest viscosity or degree of polymerization rather than those from B and C samples. Furthermore, the pulp extracted from these treatments was investigated by vibration spectroscopy and the structure differences found were validated by X-ray diffractometry. The FT-IR spectra of all pulp samples reveal the same chain conformation but different in mean hydrogen bonding, relative ether linkage and crystallinity index. From X-ray diffractograms of extracted pulp, the crystallinity index percentages for A, B and C samples were 77.0, 73.4 and 75.0 that confirm the FT-IR results.

2003-219

広葉樹材のポリサルファイド･アントラキノン添加等温蒸解の最適方法

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The most suitable method of polysulfide-anthraquinone isothermal cooking of hardwood

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Abstract: The improvement of pulp yield using a hardwood raw material, *Acacia mearnsii*, was successful in the optimization of isothermal cooking (ITC) parameters. The addition of both polysulfide (PS) and anthraquinone (AQ) gave an about 4.5-5% higher yield at kappa number of about 17. The highest yield was obtained when 70% of total active alkali and 100% of both PS and AQ were added at the beginning, and consecutively, the black liquor was exchanged with fresh white liquor containing the remaining 30% of total active alkali just after cooking temperature reached 135ºC. A mill scale trial was conducted to examine the effect of PS and AQ in a practical pulp mill. Pulp samples were collected from a continuous cooking digester not only when the PS-AQ ITC was operating but also when the simple kraft cooking was operating. Kappa number, xylose to glucose ratio, brightness and viscosity of pulps were compared between the PS-AQ ITC and with the simple kraft cooking.

2003-220

クラフトパルプ漂白工場のクロロホルムに関する環境観点からの評価

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Evaluation of chloroform formed in processes of a kraft pulp bleaching mill from the environmental aspect

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In the mill scale investigation, it was clarified that the chloroform formation in chlorine bleaching of hardwood oxygen-delignified kraft pulp (LOKP) was approximated 170 g/ pulp ton, approximated 90% of which was discharged to bleaching effluents, and that chloroform in the effluents was un- degradable in the activated sludge treatment. More than 97% of the chloroform was discharged to the air by volatilization. It is suggested that chloroform formation in Japanese LOKP bleaching

mills can be decreased to l6-42 t per one year for 8000000 t of pulp production by chorine dioxide (ECF) bleaching.

2003-221

天然から選抜した白色腐朽菌を用いた数種の環境ホルモンのバイオレメディエーション

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Bioremediation of environmental hormones by white-rot fungi screened from the nature

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Abstract: To obtain the basic information for purification of environmental hormones by bioremediation with screened fungi from the nature, degradation of two kinds of environmental hormones by fungus PL1 having ability for degradation of dioxins and with a crude enzyme from the fungus PL1 was tried in this research. *p,p*’-DDT and Lindane were used as substrates. About 72% and 64% of of *p,p*'-DDT and Lindane were degraded by the fungus in a liquid medium for 30 days, respectively. Furthermore, about 75% and 51% of *p,p*'-DDT and Lindane were degraded with the crude enzymes from the fungus in a liquid medium for 48 hours, respectively. From the results obtained here, it is suggested that bioremediation of environmental hormones like *p,p*'-DDT and Lindane by screened fungi from the nature is possible.

2003-P01

キノコ子実体フエノール性物質に関する研究

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Phenolic constituents in the mushroom fruit bodies

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Abstract: Thioacidolysis and alkaline nitrobenzene oxidation showed that typical lignin structures were not contained in the mushroom fruit bodies of *Phellinus linteus* and *Agaricus brazei* and the sclerotium of *lnonotus obliqqus*. Vanillic and syringic acids were detected in the products of alkaline hydrolysis of *lnonotus obliqqus*, but could not be obtained from the other mushrooms. The antioxidant activities of ethanol extracts

from mushrooms and sclerotium were measured by the inhibition of lipid peroxidation (ferric thiocyanate) and 1,1-diphenyt-2-picrylhydrazyl (DPPH) radical scavenging methods. The extract of *Phellinus linteus* had high activity as DPPH scavenger. and the extracts except for *Agaricus brazei* had high activities on ferric thiocyanate method.

2003-P02

細胞壁中における高分子リグニン形成過程の電顕観察

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Formation of macromolecular lignin in the cell wall as observed by electron microscope

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Abstract: In the lignifying process of xylem cell walls, macromolecular lignin is formed by polymerization of monolignols on the pectic substances, hemicelluloses and cellulose microfibrils that have deposited prior to the start of lignification. Observation of lignifying primary and secondary walls of tracheid of ginkgo by electron microscope gave images that macromolecular lignin or lignin- hemicellulose complexes are formed as modules of similar size surrounding the cellulose microfibrils. This suggests that the starting points of polymerization of lignols are distributed along the cellulose microfibri1s at almost regular intervals, 19-26 nm in the outer layer of secondary wall (S1) and 15-18 nm in the middle layer of secondary wall (S2).

2003-P03

Eucommia ulmoides Oliv.における 8-*O*-4’ネオリグナン類の生合成と立体化学：コニフェリルアルコールとシナピルアルコールとの交叉カップリング

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Biosynthesis and stereochemistry of 8-*O*-4’ neolignans in *Eucommia ulmoides* Oliv.: cross coupling of coniferyl alcohol and sinapyl alcohol

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Abstract: Four 8-*O*-4' neolignans. guaiacylglycerol-8-*O*-4'-(coniferyl alcohol) ether (GGCE); guaiacylglycerol-8-*O*-4'-(sinapyl alcohol) ether (GGSE), syringylglycero-8-*O*-4’-(sinapyl alcohol) ether (SGSE) and syringylglycerol-8-*O*-4'-(coniferyl alcohol) ether (SGCE) were synthesized. Their diastereomers were separated and elucidated by means of NMR and C_7-Hs of *threo* isomers have larger coupling constant than those of *erythro* isomer. To examine their biosynthesis, feeding experiments of *p*-[8-^{14}C]hydroxycinnamic acid and a mixture of [8-^{14}C]comiferyl alcohol (CA) and [8-^{14}C]sinapyl alcohol (SA) into young shoots of E. ulmoides were undertaken. The [^{14}C]GGCE incorporated from the former precursor was found as aglycone from stems with the *erythro/threo* ratio, 1: 1. Its glucosides from the mixed precursors were also found in stems and leaves. Incubation of a mixture of [8-^{14}C]CA and [8-^{14}C]SA with cell-free extracts from *E. ulmoides* showed the formation of not only [^{14}C]GGCE but also [^{14}C]GGSE.

2003-P04

白色腐朽菌ミノタケ由来リグニンペルオキシダーゼの反応特性 —*P. chrysosporium* 由来 LiP H8 との特性比較—

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Characterization of lignin peroxidase from the white-rot basidiomycete *Trametes cervina* -Comparison with LiPH8 from *Phanerochaete chrysosporium*

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Abstract: A possible site of veratryl alcohol (VA) oxidation in lignin peroxidase of *Trametes cervina* (TcLiP) was investigated. Reactivities of *N*-Bromosuccinimide (NBS) modified TcLiP and LiPH8 of *Phanerochaete chrysosporium* against VA were determined. VA oxidation activity of NBS-LiPH8 decreased with NBS concentration-dependent manner. On the other hand, the activity of TcLiP was not interfered by the NBS modification. Thus, the VA oxidation site of TcLiP is most likely other amino acid residue than Trp. From 3-D modeling of TcLiP, His170 is the candidate for VA oxidation site.

2003-P05
白色腐朽担子菌による Polychlorinated biphenyls の分解
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Degradation of polychlorinated biphenyls by white-rot fungi
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Abstract: We have demonstrated that white-rot fungus, *Phlebia lindtneri* has abilities to oxidize many xenobiotic compounds, such as polyaromatic hydrocarbons and dioxins. And, we have screened white-rot fungi for the degradation ability of 4,4'-dichlorobiphenyl (4,4'-DCB). As a result the strain MZ-142 was selected from twenty strains. In this study, the degradation of bipheny1 (BPE) and 4,4'-DCB by *Phlebia lindtneri* and the strain MZ-142 was examined and the mechanisms involved in initial hydroxylation were characterized. One of the metabolites, 2-hydroxy-4,4'- dichlorobiphenyl from 4,4'-DCB was identified in the culture of the both fungi during 9-day incubation. When BPE and 4,4'-DCB were treated by the strain MZ-142, the decrease of 4,4'-DCB (50%) was much higher than that of BPE (25%) in the culture of potato dextrose medium. Two kinds of metabolites, 2-hydroxy-4,4'-dichlorobiphenyl and 3-hydroxy-3,4'-dichlorobiphenyl were identified from 4,4'-DCB by the strain MZ-142. The quantity of each products was drastically dependent on the culture medium conditions. Based on these results, the specific pathway for the introduction of hydroxyl group into 4,4'-DCB by the strain MZ-142 was proposed.

2003-P06
^{14}C−コニフェリンを用いたヒヤクニチソウ管状要素におけるリグニンの標識
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Radiolabeling of lignin in secondary cell wall of Zinnia tracheary elements
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Abstract: In order to identify the protein(s) that play important roles in inhibition and/or proceeding of lignin polymerization in secondary wall, novel experimental system have been constructed with tracheary elements (TEs) of *Zinnia elegans*. In this system, lignin in the secondary wall of the *Zinnia* TEs can be labeled with ^{14}C that derived from administered coniferin-[beta-^{14}C]. The incorporated radioactivity can be estimated after thin layer chromatographic separation of thioacidolysis main monomers that recovered from ^{14}C-labeled lignin in TEs. This experimental system is useful for quantitative analysis of lignin and lignification with a small amount of cell walls.

2003-P07
キタカミハクヨウ ferulate-5-hydroxylase 遺伝子の解析
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Cloning and characterization of ferulate-5-hydroxylase gene from *Populus kitakamiensis*
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Abstract: Ferulate 5-hydroxylase (FA5H) belongs to the family of cytochrome P450-dependent mono-oxygenases. We isolated FA5H cDNA from hybrid aspen, *Populus kitakamiensis*, it was very similar to that of *Populus trichocalpa*. We prepared microsomal fraction from the transformed yeast harboring FA5H expression vector, and measured its FA5H enzyme activity. Further, we constructed expression vector for fused protein of FA5H and NADPH-cytochrome P450 oxidoreductase to increase FA5H activity.

2003-P08
赤色酵母由来 PAL 遺伝子を用いた新規薬剤耐性植物の作出
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Molecular breeding of a novel herbicide resistant plant by using phenylalanine ammonia-lyase gene from *Rodotorula rubla*

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Abstract: Phenylalanine ammonia-lyase (PAL) is a key enzyme in the secondary metabolism of higher plants. Genes encoding PAL have been identified in yeasts and plants. Amino acid sequences between plant PALs and yeast PALs have low homology and their sensitivity to aminooxy compounds, inhibitors of PAL, are very different. Yeast PALs are less sensitive. We cloned a PAL gene from *Rodotorula rubla* (RRPAL) and constructed expression vector for fused protein in *E. coli.* Further, we introduced the gene into tobacco plants. Heterogeneous expressed fused protein in *E. coli* had PAL activity and RRPAL gene were transcribed in transgenic tobacco plants.

2003-P09

ニセアカシア4CL遺伝子の単離と機能解析

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4-Coumarate : CoA ligase in *Robinia pseudoacacia*: cDNA structures

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Abstract: 4-Coumarate CoA ligase (4CL) is a key enzyme in general phenylpropanoid pathway and is believed to catalyze the activation of 4-hydroxy cinnamate analogues, however, studies indicated that most of 4CL isoenzymes are not active for sinapate. On the other hand, we reported that 4CL isoenzyme in *Robinia pseudoacacia* utilized sinapate as substrate. In this study, three 4CL cDNAs were isolated from *R. pseudoacacia* and deduced amino acid sequencess were compared to Gm4CL1 which has a catalytic activity for sinapate. A differential pattern of transcription of each Robinia 4CL gene in various organs was also investigated.

2003-P10

ダイオキシン分解菌から抽出した粗酵素による Polych1orinated Biphenyls（PCB）の分解

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Biodegradation of polychlorinated biphenyls with a crude enzyme from fungi having ability for degradation of dioxins

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Abstract: Degradations of 3,3',4,4'-tetrachlorobiphenyl(TCB) with a crude enzyme from fungus PL1 was conducted in this research to obtain basic information for purification of polychlorinated biphenyls by bioremediation with fungi screened from the nature. About 20% of TCB was degraded for 72 hours with an immobilized crude enzyme from fungus PL1 in a liquid medium. Furthermore, about 60% of TCB was degraded for 30 days with the immobilized crude enzyme from the fungus in a soil. From the results obtained here, it is suggested that bioremediation of polychlorinated biphenyls by screened fungi from the nature is possible.

2003-P11

アメリカヤマナラシにおけるシナピルアルコールデヒドロゲナーゼ（SAD）の免疫局在

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Immunolocalization of sinapyl alcohol dehydrogenase (SAD) in *Populus tremuloides*

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Abstract: To study biosynthesis of monolignols, it is necessary to know how expression and function of enzymes that ale involved in the cinnamic acid pathway are regulated. Sinapyl alcohol dehydrogenase (SAD) has been reported to catalyze the reductive reaction specifically from sinapaldehyde to sinapyl alcohol. We therefore tried to investigate the distribution of SAD in quaking aspen (*Populus tremuloides*) by immunolabeling. The labeling was mainly observed on cytosol of the differentiating xylem cells. It indicates

that sinapyl alcohol, which is the last product of monolignol, is synthesized in cytosol.

2003-P12

HBS パルプ化におけるリグニンモデル化合物の反応（2）

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Reaction of lignin model compounds during high-boiling solvent pulping (2)

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Abstract: Reaction of β-β, β-5 and β-I types of dimeric lignin model compounds were studied in 70wt% aq 1,4-butanediol solution at 180ºC to investigate the delignification mechanism under HBS (high-boiling solvent) pulping conditions. Reaction products were separated by TLC, and analyzed by HPLC, GPC and NMR. As a result, β-βand β-5 type of lignin model compounds was stable, while β-1 type is unstable and converted into stilbene. These results are in agreement with those of lignin sample.

2003-P13

HBS パルプ化におけるリグニンの構造変化　−チオアシドリシス及び NMR による解析（2）−

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Structural changes in lignin during HBS pulping -Thioacidolysis and NMR analysis (2) -

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Abstract: Structural changes in lignin during high-boiling solvent (HBS) pulping were investigated by thioacidolysis and HMQC spectra. The decrease in the content of β-*O*-4 structures was confirmed by thioacidolysis. Introduction of 1,4-butanediol into α-position of β-*O*-4 moiety was observed by HMQC spectra. The reactivity of syringyl type β-*O*-4 structure was slightly higher than that of guaiacyl type structure. The higher reactivity of syringyl type was also observed with β-1 structure. The β-1 substructure was unstable under HBS pulping conditions. Formation of stilbene structure was obvious in HMQC spectra.

2003-P14

広葉樹クラフトパルプのキシロース・グルコース比による収率予測（2）

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Prediction of pulp yields using xylose/glucose ratios of hardwood kraft pulp (2)

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Abstract: Alkali pulps were acid-hydrolyzed according to TAPPI method T249 cm-85 using 3ml of 72% sulfuric acid for 0.3g of pulp. However, it was shown that the hydrolysis is insufficient. The method was modified by the use of 6ml of 72% sulfuric acid for 0.3g of pulp and the prolonged reaction time; 2.5 hr for the primary hydrolysis. After the modified hydrolysis, the xylose ratios to glucose were obtained by gas chromatography of the alditol acetates and high performance liquid chromatography of the aldoses. Carbohydrates analysis of hardwood alkali pulps was applied to prediction of pulp yields obtained by modified polysulfide-anthraquinone pulping.

2003-P15

直接導入法による DHP の質量分析

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Mass spectrometry of dehydrogenation polymer of coniferyl alcohol with a direct sample inlet

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Abstract: A 25% tetramethylammonium hydroxide (TMAH) methanolic solution containing a bulk dehydrogenation polymer of coniferyl alcohol (DHP) was introduced into a mass spectrometer with a direct injection probe. Mass analysis employed a rate of 40ºC/m, probe temperature 50 to 400ºC, and a 70eV

ionization voltage. The mass spectrum, time integrated over scans 526-556 (225-235ºC), showed a high abundance of the m/z 181 base ion of 1-(3,4-dimethoxyphenyl)-1,2,3-trimethoxy- propane (**2**) stemming from guaiacylglycerol moieties involved in β-aryl ether linkages, and a low abundance of the m/z 386 ion, the molecular ion of pinoresinol dimethyl ether (**4**), and the m/z 370 ion, the TMAH thermochemolysis product **3** of dehydrodiconiferyl alcohol, were observed. The mass spectrum, time integrated over scans 602-639 (250-264ºC), showed a high abundance of the m/z 181 and 370 ions. The m/z 181 ion was observed ranging scans 180 from 1000 (110-370ºC). The 208 m/z molecular ion of coniferyl alcohol dimethyl ether (**1**) was observed in the spectrum integrated over scans 180-660 (110-270ºC). The mass spectrum, time integrated over scans 180-1000 (110-370ºC), was similar to the 315ºC pyrolysis mass spectrum of the DHP. TMAH thermochemolysis-gas chromatography (-mass spectrometry) of the DHP revealed GC(-MS) signals corresponding to **1**-**4**.

2003-P16

TMSiI によるリグニン β-O-4 の開裂機構の検討 —13C-標識 NMR 示差スペクトル分析法を用いて堀啓映子[*1]、新谷博幸[*1]、飯塚堯介[*1]、寺島典二[*2]

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Studies on β-O-4 cleavage by TMSiI treatment: using for ^{13}C-enriched differential NMR spectroscopy

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Abstract: Trimethylsilyl iodide (TMSiI) is known to cleave β-ether bonds selectively under very mild reaction condition. But side reactions, such as iodination and polymerization, were occurred by long time treatment. ^{13}C-enriched and unenriched DHPs were synthesized and their differential NMR spectra were measured before and after TMSil treatment in NMR tube. The differential NMR spectra showed some changes indicating decreased amount of β-O-4, coniferyl alcohol and coniferaldehyde structures and appearance of one signal after TMSil treatment. However, total peak area was also decreased after TMSiI treatment, probably because of the precipitation of reaction products by water addition for stopping the reaction. Water addition might cause some side reactions.

2003-P17

単離過程におけるリグニン構造の変化とその要因について —磨砕処理の影響—

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Changes of lignin structures during the process of MWL isolation

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Abstract: Milled wood lignin (MWL) is a lignin sample that reflects the characters of protolignin in wood, although it is well recognized that MWL represents only a part of protolignin and it can never be free from structural modification during its isolation procedure. The structures of MWL are featured by such artificial changes and native differences, in addition to general characteristics as lignin. In this paper, we aimed to distinguish the nature of lignin after milling from its original nature by the use of alkaline nitrobenzene oxidation method and determination of methoxyl groups in order to understand the essential characters of MWL and lignin in wood and milled wood. From the results of S/V ratios and the yields of main oxidation products by alkaline nitrobenzene oxidation, it was suggested that the nucleic structural differences in crude MWLs might reflect mainly the native differences in lignin.

2003-P18

アルカリ性酸素脱リグニン段排液リグニンの土壌改良剤としての性状

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Characterization of lignin fractions in alkaline-oxygen stage waste liquor as soil conditioning agent

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Abstract: In most of the worlds tropical areas where soil is acidic, Al toxicity is a serious problem which limits the productivity of crop plants. The possibility of utilizing lignin fragments from alkaline oxygen

delignification stage waste liquor generated from paper mill as soil conditioning agent was studied. Alkaline oxygen delignification stage waste liquor was subjected to Gel Filtrationn Chromatography (GFC) and separated into four fractions (F1, F2, F3, and F4). Then, these four fractions were used for plant experiment. The results indicated lignin fragments are capable of alleviating the toxicity of Al, providing improved performance of radish root growth. Each fraction showed different performance on removing the Al toxicity, and so the reason for their different behaviors on Al toxicity was also studied.

2003-P19

スギおよびブナの超臨界水処理により得られるリグニン由来物質の GC−MS 分析

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Gas chromatographic and mass spectrometric (GC-MS) analysis of lignin-derived products from *Cryptomeria japonica* and *Fagus crenata* as treated in supercritical water

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Abstract: Softwood (*Cryptomeria japonic*) and hardwood (*Fagus crenata*) were treated in supercritical water (380ºC, 100MPa) for 8 seconds. The treated woods were fractionated to the water-soluble portion, methanol-soluble portion and methanol-insoluble residues. For the methanol- soluble portion which mainly consists of lignin-derived products, GPC and GC-MS analyses were made to clarify the molecular weight distribution and to identify monomeric products, respectively. GPC analysis revealed that the methanol-soluble portion contains monomeric and some oligomeric products. Nineteen guaiacyl compounds in methanol-soluble portion from softwood, and 15 syringyl compounds in methanol-soluble portion from hardwood were identified by GC-MS analysis. These observations suggested that the lignin-derived products are useful products for substituting the chemicals from fossil resources.

2003-P20

中性抄紙における硫酸リグニン由来のロジンサイズ定着剤の調製とその評価

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Preparation and evaluation of retention aids for rosin sizes from sulfuric acid lignin in neutral papermaking condition

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Abstract: Cationic polymers as the retention aids for rosin sizes in neutral papermaking were prepared from sulfuric acid lignin (SAL), one type of acid lignin. To convert SAL to the cationic polymer (MP-SAL), SAL was phenolated followed by the Mannich reaction to introduce the amino groups. In the MP-SAL single system, MP-SAL exhibited high sizing effectiveness in neutral papermaking with the rosin emulsion size. However, MP-SAL showed no sizing effectiveness when soap rosin size was used. In the alum-MP-SAL dual system, alum and MP-SAL, synergistically enhanced the sizing effectiveness in the rosin emulsion sizing at neutral pH.

2003-P21

ヒドロキシプロピル化未漂白パルプより調製したゲルの膨潤挙動

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Swelling behavior of hydroxypropylated unbleached pulp gels

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Abstract: Urethane- and epoxy-types of gels were prepared from hydroxypropylated unbleached acetic acid pulps (HP-AP' s) using hexamethylen diisocianate (HDl) and ethyleneglycol diglycidyl ether (ED) as cross-linkers. The residual lignin content influenced thermoresponse of the gels; the volume-transition temperature of the gel upon heating was lowered by the lignin. The epoxy-type gel from HP-softwood AP showed the volume transition at 38ºC, suggesting its possibility as a support in the drug delivery system. In addition, all the gels showed very unique swelling behavior in aqueous solution of cationic surfactants. Although the mechanism have not been clarified yet, the behavior seems to contribute to explore novel utilization of the gels.

2003-P22

リグニンゲルの膨潤と応用

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Swelling mechanism and application of lignin gel

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Abstract: Lignin-gel was prepared from acetic acid lignin (AL) with polyethylene glycol diglycidyl ether (PE) at a high lignin concentration. This lignin gel was found to swell in aqueous organic solvents. The mobility of the solvated solvent was evaluated from the spin-spin lattice relaxation time (T_2) using NMR to clarify the swelling mechanism. T_2 of the solvents decreased with increasing the gel swelling degree. In particular, this tendency of the organic solvent was remarkable. This result suggests that the adsorption of solvent molecules onto gel polymer chain reduces the mobility of the solvent. As one of the applications of lignin gel, we attempted to utilize it as a membrane for solvent separation by pervaporation. As a result, ethanol selectively permeated at the low ethanol concentration, but the selectivity changes at the high concentration.

2003-P23

リグノスルホン酸塩系ポリウレタンゲルの調製と物性

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DSC and AFM studies on sodium lignosulfonate-based PU hydrogels

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Abstract: Sodium lignosulfonate (LS)-based polyurethane (PU) hydrogels were prepared from LS and hexamethylene diisocyanate (HDI) derivatives. Water content (Wc) of the obtained PU hydrogels was less than 3.0 $g\ g^{-1}$ and NCO/OH ratio was varied from 0.2 to 0.6 $mol\ mol^{-1}$. Phase transitions of LS and PU hydrogels were measured by differential scanning calorimetry PSC). From DSC curves, glass transition temperature (T_g), melting peak at low temperature (T_{ml}) and melting peak at high temperature (T_{mh}) were observed. It was also confirmed that there were three kinds of water, non-freezing water, freezing bound water, and freezing water.

2003-P24

アルコリシスリグニン、エチレングリコール及びグリセリンのエステル—カルボン酸誘導体を原料とするエポキシ樹脂の合成とその熱的性質

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Synthesis and thermal properties of epoxy resins from ester-carboxylic acid derivatives of alcoholysis lignin, ethylene glycol and glycerin

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Abstract: Alcoholysis lignin (AL) was dissolved in ethylene glycol (EG) and the obtained mixture was reacted with succinic anhydride to form a mixture of ester-carboxylic acid derivatives (AL-EG polyacid, ALEGPA). Glycerin-polyacid (ALGLYPA) was also prepared from AL and glycerin. The mixture of ALEGPA and ALGLYPA was reacted with ethylene glycol diglycidyl ether in the presence of catalytic amount of dimethylbenzylamine to form epoxy resins. The molar ratio of epoxy groups to carboxylic acid groups ([EPOXY]/[AA] ratios, mol/mol) was maintained at 1.1. The contents of ALGLYPA in the mixture of ALEGPA and ALGLYPA (ALGLYPA content) were varied from 0 to 100 %. Thermal properties of epoxy resins were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG). Glass transition temperatures (T_g's) of epoxy resins increased with increasing ALGLYPA contents suggesting that glycerin structure acts as a hard segment in epoxy resin networks. Thermal decomposition temperatures (T_d'S) of epoxy resins were almost constant regardless of ALGLYPA contents.

2003-P25

クラフトリグニン及びリグノスルホン酸塩系木粉分散型ポリウレタン複合材料の熱的・機械的性質

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Thermal and mechanical properties of PU composites containing wood powder with sodium lignosulfonate and kraft lignin

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Abstract: Polyurethape (PU) composites were prepared from ground wood mixed with a kraft lignin (KL)-polyol solution and sodium lignosulfonate (LS)-polyol solution consisting of KL or LS dissolved in polyethylene glycol (PEG-200) triethylene glycol (TEG) and diethylene glycol (DEG). Mechanical and thermal properties of the above composites were studied. Thermal properties of the prepared PU composites were studied by thermogravimetry (TG). Sample weight for TG was ca. 7mg. Mechanical properties of PU composites were studied by compression tests, according to the Japanese Industrial Standard (JIS) A 1408 at room temperature.

2003-P26

無機粒子分散型クラフトリグニン系ポリウレタンの調製と物性

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Mechanical properties of kraft lignin-based PU foams containing inorganic fillers

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Abstract: Rigid polyurethane (PU) foams were prepared from kraft lignin (KL) which was dissolved in diethylene glycol (DEG), triethylene glycol (TEG) or polyethylene glycol (molecular weight 200: PEG200). The obtained solution containing filler was reacted with isocyanate in the presence of small amounts of silicone surfactant, catalyst and water. Mechanical properties of these polyurethanes (PU's) were studied by compression tests. It was found that compression strength and compression elasticity of KLPU show maximum values at a certain filler content from 10 to 40%. Compression strength decreased with increasing molecular weight of ethylene glycol.

2003-P27

植物性廃棄物に由来するリグニンの油脂に対する参加防止効果

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Antioxidant effect of lignin obtained from botanical wastes

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Abstract: Antioxidant effect of lignin and lignophenol, which were prepared from botanical wastes, was investigated. As the botanical wastes, used tea leaves (green tea), peanut husk, rice bran, and wood meal were used. The antioxidant effect was evaluated on the basis of the changes in peroxide value by auto-oxidation of linoleic acid. It was found that all samples showed high antioxidant effect. Especially, a lignophenol from tea leaves had the highest activity. In comparison with commercially available antioxidants, the antioxidant effect of the lignophenol from tea leaves was higher than that, of vitamin E, but lower than those of t-butylhydroxyanisol (=BHA) and ferulic acid.

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2004-101

表面プラズモン共鳴を用いたモノリグノール類とヘミセルロースの相互作用解析

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Investigation on interaction between monolignols and hemicellulose using surface plasmon resonance
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Abstract: Interactions of monolignol (coniferyl alcohol) or its glucoside (coniferin) with xylan was investigated by the surface plasmon resonance (Biacore^{TM}) to clarify the transportation of lignin precursor from cytoplasm in the lignification process. Xylan isolated from birch was oxidized with periodate to generate aldehyde group, and then the resulting xylan was immobilized onto carboxymethyl (CM)-dextran as a support of sensor chip by the reductive amination to give a ligand on the sensor chip. The adsorption capacity of the oxidized xylan to coniferin was much larger than that of its glucoside. It is proposed that coniferyl alcohol would be supplied from cytoplasm for lignification but not its glucoside.

2004-102

広葉樹放射組織におけるリグニン化学構造の特性について

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Structure of lignin in ray parenchyma obtained by a direct sampling without chemical treatment
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Abstract: 'Ray' and 'ray-free' fractions were separated from heartwood of *Platanus orientalis* by direct cutting on naked eyes. Klason lignin content was higher in 'ray' and lower in 'ray-free' fraction. Diastereomer ratio of β-O-4 structure obtained by ozonation method (E/T ratio) and ratio of aromatic ring type obtained by nitrobenzene oxidation (S/V ratio) were also higher in 'ray' and lower in 'ray-free' fraction. These tendencies were the same as those in sapwood. However, both S/V and E/T ratios obtained for whole wood of heartwood didn't exhibit the intermediate values of 'ray' and 'ray-free' fraction of heartwood. Although this result can't be explained at this moment, it was implied that alcohol-benzene extractives could affect significantly the results of nitrobenzene oxidation and ozonation. When all values of E/T ratio obtained in this experiment were plotted against those of SN ratio, they were correlated well each other, which confirmed the recent finding by Akiyama et al.

2004-103

高分子鋳型存在下でのコニフェリルアルコールの酵素重合

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Enzymatic polymerization of coniferyl alcohol in the presence of polymer templates
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Abstract: Dehydrogenative polymerisate (DHP) of coniferyl alcohol, a main monomer of lignin, was prepared by the use of horseradish peroxidase/H_2O_2 system in the presence of polymer templates, e.g., poly(ethylene glycol), cellulose, xylan, and cyclodextrins (CDs). DHP was characterized by ^{1}H NMR and size exclusion chromatography. The chemical bonds ratio (β-O-4': β-5': β-β') was calculated by using the signal of ^{1}H NMR of acetylated DHP. Addition of xylan and α-CD led to the increase of β-5' and β-O-4' structure, respectively. This result indicated that chemical structure of DHP was regulated by the additions of xylan and α-CD in the reaction medium.

2004-104

細胞壁中における高分子リグニン形成過程の電顕観察　III. イチョウの Purves リグニンの観察

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Formation of macromolecular lignin in the cell wall as observed by electron microscopy III, Observation of

Purves lignin prepared from differentiating xylem of *Ginkgo biloba*

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Abstract: In the lignifying cell wall, lignin is formed as beads-like modules of lignin-hemicellulose complexes surrounding cellulose microfibrils as observed by FE-SEM. It was assumed that fusion of the modules in a final stage of cell wall lignification form a super high-molecular lignin-hemicellulose complex. Purves lignin was isolated from the differentiating ginkgo xylem by selective removal of polysaccharides by periodate oxidation. The lignin retained morphological features of tracheids even if it is isolated from the wood in which phenolic hydroxyl groups of lignin were protected by methylation from undesirable modification during periodate oxidation. The results support the assumed ultrastructural assembly of the cell wall polymers in ginkgo tracheids.

2004-105

イソコニフェリン化学合成法の改良とその脱水兼重合

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lmprovement of chemical synthesis of isoconiferin and its dehydrogenative polymerization

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Abstract: To obtain highly polymerized DHP (Dehydrogenation polymer) by an introduction of hydrophilic glucose unit to monolignol, isoconiferin was successively prepared by the use of imidate method and polymerized by Peroxidase/ Hydrogen peroxide. The polymerization of isoconiferin proceeded in a completely homogeneous way and the resulting polymer was water-soluble. The molecular weight of isoconiferin-DHP depended on monomer addition times, concentrations of monomer and most strongly on amounts of peroxidase, while the molecular weight of coniferyl alcohol-DHP had no dependence on the amount of Peroxidase. As the results, maximum DP of isoconiferin-DHP was 31, while that of comiferyl alcohol was 15.

2004-106

β-O-4 型規則性人工リグニンポリマーの合成（2）

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Synthesis of artificial lignin polymer composed of β-*O*-4 structure

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Abstract: The β-*O*-4 structure is one of the most important substructures in lignin. We are working on the synthesis of lignin polymers composed of only β-*O*-4 structure from simple aromatic compounds as starting materials by a solution polymerization method. New monomer was selected and polymerized in the presence of alkali. The obtained polymeric material was analyzed by ^{1}H- and ^{13}C-NMR spectroscopy, which suggests that the polymer has a regular structure. Molecular weight of the polymer will be determined by GPC analysis.

2004-107

ポプラペルオキシダーゼ遺伝子の単離とそれらのストレス誘導発現解析

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Isolation and expression analysis of peroxidase genes in poplar under stress treatments

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Abstract: In higher plants, the peroxidase (PO) activity is generally upregulated by environmental stresses. However, PO comprise a multigene family, and therefore the most of physiological functions of isoenzynes have yet been unclear. In this Study, we analyzed the gene expression of some POs from poplar, a model tree. ESTs generated from the stress-treated leaves of *Populus nigra* were subjected to the screeming of poplar PO clones, and 198 PO candidates were isolated. Of the 198 candidates, we selected 11 PO clones. A cationic PO clone was abundantly expressed in the poplar stress-related ESTs (104/198), suggesting its stress inducibility. In fact, it was confirmed to be induced by environmental stress treatnents such as dry, cold, heat, and H_2O_2 by northern

analysis. The exhaustive expression analysis of other PO genes and additional 17 PO clones isolated from the leaf, shoot, and xylem of *P. alba* with respect to the stress-induction is now undergoing.

2004-108

LIM様転写因子の発現抑制による低リグニン樹木の開発

河岡明義，渡邊恵子，南藤和也，海老沼宏安

日本製紙株式会社森林科学研究所

Production and characterization of lignin-reduced woody plants by suppression of LIM transcription factor

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Abstract: Lignins are phenolic polymers that are embedded in the cell walls of specialized plant cells. Our research purpose is to produce woody plants with low level of lignin for environmental and economical benefits of pulp production. Previously, we identified a cDNA encoding transcription factor from tobacco (*Nicotiana tabacum*), namely Nt1im1 that regulates the gene expression involved in lignin biosynthesis. The antisense Nt1im1construct was introduced into *Eucalyptus camaldulensis* that is one of the most important hardwood for afforestration. The transgenic Eucalyptus grown in the greenhouse showed 5% reduction of lignin content and 5% increase of holocellulose content.

2004-109

リグナンの位置選択的メチル化を触媒する新規 *O*-メチルトランスフエラーゼ

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A novel *O*-methyltransferase catalyzing a regioselective methylation of lignan

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Abstract: In spite of frequent occurrence of methoxyl groups in lignan molecules, little is known about *O*-methyltransferases (OMTs) involoved in lignan *O*-methylation. The present study reports the isolation of a novel safflower (*Carthamus tinctorius*) gene encoding a lignan *O*-methyltransferase which catalyzes regioselective methylation of matairesinol giving rise to arctigenin, but not isoarctigenin. A recombinant protein of the enzyme, matairesinol *O*-methyltransferase (CtMROMT),

expressed in *E. coli,* exhibited the regioselectivity, like the plant protein, while the recombinmt CtMROMT did not catalyze *O*-methylation of hydroxymonolignols and cinnamates, suggesting that the OMT is a novel type of plant OMT specific to lignan methylation.

2004-110

トチュウ粗酵素によってコニフェリルアルコールから生じる(＋)-エリトロ-及び(−)-トレオ-グアイアシルグリセロール−β−コニフェリルエーテルの絶対立体配置とその新奇な立体選択的生成機構の提案

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Absolute configuration of (+)*erythro*- and (-)-*threo*-guaiacylglycerol-β-coniferyl ethers formed by the incubation of coniferyl alcohol wit cell-free extracts of *Eucommia ulmoides* and their novel stereoselective formation

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Abstract: Incubation of coniferyl alcohol wit cell-free extracts of *Eucommia ulmoides* in die presence of hydrogen peroxide gave (+)*erythro*- and (-)-*threo*-guaiacylglycerol-β-oniferyl ethers (GGCE), and the *erythro* isomer was formed more than the *threo* isomer. Absolute configuration of (+)*erythro,* (-)*erythro*, (+)-*threo*, and (-)-*threo* GGCE was determined as (7R, 8S), (7S, 8R), (7S, 8S), and (7R, 8R), respectively, by Mosher's method. Quanbtative analysis of the four stereoisomers, (7R, 8S)-(+) *erythro*-, (7S, 8R)- (-)*erythro*-, (7S, 8S)-(+)-*threo*-, and (7R, 8R)-(-)-*threo*-GGCE, showed that their percentages were 44.45%, 25.55%, 5.25%, and 24.75%, respectively. We found for die first time an enzyme activity that catalyzes the stereoselective addition of water to (8R)-quinonemethide giving (7R, 8S)- (+)-*erythro*-GGCE. Non-enzymatic addition of water to the (8S)-quinonamethide gave (7S, 8R)-(-)*erythro*- and (7R, 8R)-(-)*threo*-GGCE in the almost same ratio.

2004-111

Evolution of lignin —Structural characteristics of polyphenolic components of bryophytes pteridophytes and spermatophytes

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Abstract: Polyphenolic components of several species of bryophytes and pteridophytes, which have been gifted by Dr. T. Ishii, Forestry and Forest Products Research Institute and Dr. M, Higuchi, National Science Museum, were examined by the yield of residues after Klason treatment. an alkaline nitrobenzene oxidation for aromatic composition, analytical ozonolysis to investigate the presence of β-O-4 intermonomer linkages and methoxyl content. Syringyl unit was detected in alkaline nitrobenzene oxidation products of *Selaginella tamariscina* (Beauv.) Spring and molar ratio of syringyl to guaiacyl nuclei (S/V ratio) was 2.31. Björkman lignins were prepared from *S. tamariscina* and *Polystichum polyblepharum* after extraction with 80% EtOH followed by water to investigate structural characteristics of lignins. The presence of syringyl unit as the major component of lignin in *S. tamariscina*, but not in *P. polyblepharum*, was also supported by ^{1}H NMR and FTIR spectroscopies,

and confirmed by acidolysis and ozonation, that syringyl unit of *S. tamariscina* lignin is involved in β-O-4 linkages. The low content of methoxyl group and low total yield of alkaline nitrobenzene oxidation products and ozonation products suggest that Klason residue is not represent real lignin of
S. tamariscina and *P. polyblepharum*.

2004-112

β-O-4 型構造の側鎖の立体構造を規定する要因(その 2)—*erythro/threo* 比と S/V 比の相関—

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[*1] 東京大学院農学生命科学研究科、[*2]Bogor Agricultural University

A factor determining the diastereomeric forms of β-O-4 structures -Relationships between *erythro/threo* ratio and syringyl/guaiacyl ratio among different wood species

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Abstract: Twenty-one wood species containing softwoods and hardwoods were subjected to nitrobenzene oxidation. The S/V ratio obtained was widely varied depending on wood species (0 to 6.1). The *erythro*/(*erythro* + *threo*) ratios of β-O-4 structures were strongly correlated with the S/(S+V) ratios ($R^2 = 0.99$), as well as with the previously reported methoxyl group content in lignin ($R^2 = 0.83$). It was suggested that syringyl/guaiacyl composition is one of the factors which control the proportion of *erythro* and *threo* forms of β-O-4 structures during the process of lignin formation. By nitrobenzene oxidation, a variation in the content of biphenyl type (5-5 linkage type) structure was also investigated based on divanillin yield.

2004-特別講演

リグニン科学の新たな展開 —リグニン科学者に求められている課題—

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Let's advance a fresh lignin science: Assignments asked for lignin scientists

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Tokyo University of Agriculture and the University of Tokyo

Abstract: The most abundant organic compound on the earth is "Lignin", but not cellulose, because lignin resists strongly against mineralization by the activities of microorganisms. Presence of lignin, therefore, plays a key part in global carbon circulation, global environment and accumulation of fossil resources. In addition, the term of lignin is discussed widely in various disciplines such as agricultural science, botany, environmental science, ecology, animal husbandry, pharmacy, oceanography, archaeology, and so on. Lignin scientists are looked forward to advancing such disciplines. The assignments asked for lignin scientists are discussed.

2004-201

Phanerochaete crassa WD1694 菌の菌糸先端部のペルオキシダーゼ活性の定量

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Extracellular peroxidase activity at the apical tip of *Phanerochaete crassa* WD1694

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Abstract: Extracellular peroxidase activity of *Phanerochaete crassa* WD1694 was visualized by staining with a peroxidase substrate, 3,3'-5,5'-Tetramethylbenzidine precipitate. The staining occurred directly on and along the apical tip of the mycelium. Visible spectra and absorbance of the staining at the apical tip was analyzed by microspectrophotometry, and catalytic velocity was calculated. The maximum catalytic velocity was estimated 1135□M/min. The result clearly showed that the catalytic velocity of the extracellular peroxidase reaction at the apical tip of *P. crassa* WD1694 was much higher than that reported on MnP and Lip of *Phanerochaete chrysosporium* that caused the depolymerization of lignin in vitro.

2004-202

^{13}C シアン配位型ペルオキシダーゼの NMR 解析 —過酸化水素との反応における活性部位アミノ酸残基の役割—

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NMR Analysis of ^{13}C^{15}N-ligated lignin peroxidase and manganese peroxidase - Role of active-site amino acids in hydrogen peroxide activation

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Abstract: To investigate the heme environment of lignin peroxidase and manganese peroxidase from *Phanerochaete chrysosporium*, ^{13}C- and ^{15}N-NMR spectroscopjc techniques were utilized. ^{13}C-NMR signals of cyanide bound to the heme iron of LiP and MnP (-3860 ppm and -3863 ppm , respectively) indicated that electron push effect from axial ligands of both enzymes were much lower than that of common peroxidases, e.g. horseradish peroxidase. On the other hand, ^{15}N-NMR analysis of these enzymes revealed that the electron pull effect of both enzymes were strong as observed in other peroxidases. These results indicated that LiP and MnP were shown to share unique features, significantly weak electron push effect but with strong pull effect, which may explain slower rates of compound I formation for either LiP or MnP.

2004-203

Phanerochaete chrysosporium におけるパスウェイクロストーク

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Pathway crosstalk involved in lignin degradation system of *Phanerochaete chrysosporium*

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Abstract: A proteomic analysis for surveying heme-binding proteins produced by the white-rot basidiomycete *Phanerochaete chrysosporium* was performed utilizing a biotinylated heme- streptavidin beads system. Mitochondrial citrate synthase (CS) and glyceraldehyde 3-phosphate dehydrogenase (GAPDH) were identified as a heme binding protein. CS was shown to possess a Cys-Pro motif, a well-known heme responsive motif, in its amino acid sequences. A homology modeling via MOE using the crystal structure of citrate synthase from pig as a template revealed the existence of the Cys-Pro motif on the surface of the protein. A genomic analysis revealed that 5-Aminolevulinic acid synthase (ALAS) also possesses the Cys-Pro motif. These data, combined with our previous data showing the involvement of CS, GAPDH, and ALAS in the metabolic control of carbon flux and redox regulation, strongly suggested that the existence of a unique pathway crosstalk between the glycolysis, TCA cycle, and heme biosynthetic pathway. This pathway crosstalk is thought necessary for optimizing fungal lignin degradation system.

2004-204

多糖加水分解酵素による MWL 抽出残渣の分解挙動(II) —特にキシラナーゼ処理について—

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The behavior of degradation of wood meal after extraction of the MWL by carbohydrate-degrading enzymes (II) -Structural analysis by xylanase
Hiroyuki Furuno, Hiroshi Kamitakahara, Toshiyuki Tbkano, Fumiaki Nakatsubo
Graduate school of Agriculture, Kyoto University

Abstract: The xylanase treatment of Cellulose-Lignin fracdon (CL), which was extracted from MWL extracted residue with LiCl/ DMAc, was carried out. From neutral sugar and lignin analyses data, it was found that xylanase sohbilized approximately 75% of xylose and 41% of lignin CL. From GPC data, it was found that the molecular weight of the solubilized lignin was much lower than MWL. These indicated that no less than 40% of lignin in CL, with a low molecular weight, formed xylan-lignin complex. The solubilized lignin apparently had the native structure derived from LCC.

2004-205
酸素アルカリ処理におけるクラフトリグニンの酸素消費量の測定
今井愛子、友日生織、松本雄二，飯塚堯介
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Accurate measurement of oxygen consumption during oxygen-alkali treatment of kraft lignin and lignin model compounds
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Abstract: During oxygen-alkali bleaching, the progress of lignin oxidation is believed to govern the delignification. However there seems to be no clear relationships established between the oxidation reaction and delignification. In order to directly analyze the progress of lignin oxidation, we designed a measuring device by which oxygen consumption can be precisely followed based on the accurate measurement of oxygen supply to the reactor. By use of this device, oxygen consumption of isolated softwood kraft lignin and several lignin model compounds was measured under 0.80 MPa of oxygen pressure at 95ºC. The results were that one aromatic ring consumed about 3 oxygen molecules. Although non-phenolic lignin model compound didn't consume any oxygen, results obtained for kraft lignin suggested that non-phenolic unit as well as phenolic unit in lignin consumed oxygen during oxygen-alkali treatment.

2004-205
化学パルプの温和なアルカリ処理による過マンガン酸カリウム消費物質の生成
友田生織、童国林、松本雄二、飯塚堯介
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Formation of permanganate consuming substances by mild alkali treatment of chemical pulp
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Abstract: Permanganate consuming structures were produced from kraft pulp by mild alkali treatment. Its formation was suppressed when hydrogen peroxide was present during the reaction. In order to fully understand the role of hydrogen peroxide, pulp was treated by alkali in the presence or absence of hydrogen peroxide under different pH and the permanganate consumption of both pulp and reaction liquor were analyzed. As roles of hydrogen peroxide, (i) destruction of permanganate consuming structures, (ii) suppression of the formation of permanganate consuming structures, and (iii) prohibition of incorporation of permanganate consuming structures into pulp were suggested.

2004-207
リグニンの嫌気条件件下での微生物変性 —シロアリ原腸を通過したリグニンの性状—
勝亦京子[*1]、堀啓映子[*1]、飯山賢治[*2]
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Changes in structural feature of lignin by microorganism under anaerobic condition -Property of lignin after digestion by termite
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Abstract: Behavior of biodegradation (biomodification) of plant cell wall components under aerobic condition is well documented, but not enough for especially lignin under anaerobic system. Biomodification of lignin is greatly due to the activities of peroxidase group, it is not clear yet the behavior of peroxidases under anaerobic condition. Digestion of woody materials by termites is the typical anaerobic modification of plant cell wall components together with digestion of forages in rumen of ruminants. Changes in chemical feature of lignin by microorganism under anaerobic condition were investigated by the comparison of cell wall components of wood before and after digestion by termite. Wood of Ilang-Ilang (*Ilang-Ilang C. dadloyl*) and Apitong (*Dipterocarpus grandiflorua*) and excrements of termites which feed each wood were collected from University of the Philippines. Los Baňos. Björkman lignin of each samples were isolated. There were no significant differences on ^{1}H-NMR spectra between acetylated Björkman lignin from excrements and original woods. Methoxyl contents of Björkman lignins from excrements of termite were also similar to those of original wood. Small differences for only contents of aliphatic hydroxyl and conjugated phenolic hydroxyl group were detected.

2004-208
リグニンエーテル構造の熱分解開裂機構
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Mechanism of the pyrolytic cleavage of ether structures in lignin
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Abstract: Mechanism of the pyrolytic cleavage of α- and β-ether structures in ligmin was studied with α-ether types of dimeric and α, β-diether types of trimeric model compounds having differently substituted Cα-phenyl ether groups. As a result, phenolic and non-phenolic α-ether structures were cleaved in ionic and homolytic (radical) mechanisms, respectively, in dimers. In trimers, additional β-ether groups did not change the mechanism of the α-ether cleavage of the non- phenolic trimers, wheras the ionic mechanism was changed to radical in the phenolic trimers. The latter results are reasonably explained with the formation of radical species through homolytic cleavage of the β-ether structure, although the pyrolytic cleavage of the phenolic α-ether structures in the phenolic trimers is initiated with the ionic mechanism.

2004-209
木材の光劣化（II）—光照射によるスギ材表面のリグニン構造変化—
砂原　寛[*1]、中川明子[*2]、富田文一郎[*2]、黒田健一[*3]
[*1] ケミプロ化成株式会社、[*2] 筑波大学大学院生命環境科学研究科、[*3] 九州大学大学院農学研究院
Photodegradation of wood (2) -Change of lignin structure of *Cryptomeria japonica* D. Don by UV irradiation
Hiroshi Sunahara[*1], Akiko Nakagawa[*2], Bunichiro Tomita[*2], Ken-ichi Kuroda[*3]
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University

Abstract: When lumber is left for out side for long time, the color of the lumber's surface is changed, yellow to white-brown and the surface was cracking. These are due to the participation of photo degradation of lignin by UV irradiation. We then started to the study of photo degradation of lignin. The results suggested that lignin is degraded early time (acceleration by UV irradiation for 1 to 5 hours). A decrease in β-O-4 subunits was found by pyrolysis gas chromatography.

2004-210
リグニン含有フエノール樹脂の表面特性
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Surface characteristics of phenol resins contained lignin
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Abstract: The surface characteristics of phenol-formaldehyde (PF) resin with lignosulfonate and kraft lignin were determined by contact angle measurement and inverse gas chromatography (IGC). In the contact angle measurement, the three-liquid method was utilized to determine the Lifshitz- van der Waals components (γ^{LW}), electron-acceptor parameter (γ^+), and electron- donor parameter (γs^-) of the prepared resins and calculation of the acid-base component of the work of adhesion between water and the resins. The result of IGC

showed the same γ^{LW} trends obtained from the contact angle measurement.

2004-211

セルロース微粒子充填クラフトリグニン系エポキシ樹脂複合材料の製造

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産業技術総合研究所

Preparation of composites of kraft-lignin based epoxy resin filled with cellulose particle

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Abstract: A mixture of ester-carboxylic acid derivatives (KLPA) was obtained by reaction of an ethylene glycol solution of Kraft 1ignin (KL) and succinic anhydride in the presence of a catalytic amount of dimethylbenzylamine at 80 ºC. Composite samples were prepared by a reaction of the mixture of KLPA and cellulose particles with ethylene glycol diglycidyl ether (EGDGE) at 70 ºC. Cellulose contents ranged from 0 to 60 wt%. The above mixtures were molded into sheets at 130 ºC for 5 hours. The mechanical properties of the samples were investigated by tensile tests using plate type specimens.

2004-212

断熱材用リグニンベースポリウレタンフォームの熱的機械的性質

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Thermal and mechanical properties of lignin-based rigid polyurethane foams for insulation

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Abstract: Rigid polymethane (PU) foams for insulation were prepared from various kinds of lignins such as kraft lignin (KL), sodium lignosulfonate (LS), solvolysis lignin (SL) and alcoholysis lignin (AL). Thermal and mechanical properties of the above polyurethane foams (PU's) were investigated by differential scanning calorimetry (DSC), thermogravimetry (TG), and compression tests. It was found that glass transition emperatures (T_g's), thermal degradation temperatures (T_d'S) and mechanical properties of the PU's were not prominently dependent on kinds of lignin and that all of the above lignin-based PU's are available for insulation. From the viewpoints of practical utilization, KL- and LS-based PU's were compared in this study.

2004-213

リピッドペルオキシデーションにおけるリグニン分解のラジカル反応化学的考察 —カーボンセンターラジカルについて

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Radical chemistry of lipid peroxidation for lignin degradation: On the roles of carbon-centered radicals

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Abstract: In 1999, Kapich et al. reported that peroxyl radicals produced by thermal decomposition of azo compounds degraded a non-phenolic lignin model compound. However, there was no direct evidence showing that carbon-centered radicals were responsible for the degradation. In the present study, mechanisms for the non-phenolic β-*O*-4 lignin model degradation by carbon-centered radicals from azo compounds were investigated. The results suggested that carbon-centered radicals are able to degrade the model compound by a mechanism different from that for peroxyl radicals.

2004-214 カワラタケによるフタル酸ジブチルの分解とそれに関与する酵素

山田喜彦、平井浩文、河合真吾、西田友昭
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Degradation of di-*n*-butyl phthalate by white rot fungus *Trametes versicolor* and its related enzyme

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Abstract: Di-*n*-butyl phthalate (DBP) is widely used in a variety of industrial applications as a plasticizer, and is suspected of having estrogenic (endocrine- disrupting) activity, mutagenicity, teratogenicity, and carcinogenicity. In this study, therefore, we attempted the degradation of DBP by white rot fungus *Trametes versicolor*. DBP decreased by 85% and 95% after 2 days and 3 days of fungal treatment, respectively, and DBP was converted into mono-*n*-butyl phthalate (MBP) and an unidentified product. Although no appreciable decrease of DBP was obtained by manganese peroxidase and laccase, the cell-free extract prepared from the mycelium of *T. versicolor* decreased DBP and converted DBP into MBP. This result indicated that the intracellular enzyme(s) produced by white rot fungus is involved in DBP degradation.

2004-215

白色腐朽担子菌とその菌体外酵素による異常プリオンタンパクの分解

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Biodegradation of protease-resistant prion protein by white-rot fungi and their ligninolytic enzymes

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Abstract: Protease Resistant Prion Protein (PrP^{Res}) is cause substance of bovine spongiform encephalopathy (BSE) and other diseases. PrP^{Res} can not be degraded either by proteases or usual chemical treatments. Thus, validated method for the decontamination of PrP^{Res} is urgently required. Recently, white-rot fungi have received worldwide attention for bioremediation because of their abilities for the degradation and detoxification of environmental pollutants, such as dioxins and chlorophenols. In this study, PrP^{Res} was treated by 14 white-rot fungi and 1 brown-rot fungus. The PrP^{Res} was completely degraded by 8 white-rot fungi, and all these fungi produced manganese peroxidase (MnP) during the treatment. The crude extracellular enzyme also degraded PrP^{Res} in the condition containing Mn(II) and H_2O_2. These results support that MnP is a key enzyme for PrP^{Res} degradation.

2004-P01

LCC の両親媒的性質

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Amphiphilic characteristics of LCC

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Abstract: Lignin-Carbohydrate Complex (LCC) was isolated from wood meal residue with DMSO after extraction of milled wood lignin (MWL). Transmission electron micrographs after negative staining indicated that LCC formed self-aggregates in water with diameters in the range of nano-meter. The aggregates revealed to have strong hydrophobic domains by the fluorometric study of their complexes with fluorescent reagents as indicators for hydrophobicity. The surface pressure (π)-area (A) isotherms of LCC also indicated self-assembly and the possibihty of formation of LB film.

2004-P02

リグニン・炭水化物結合体の単離（IV)アカマツ材からの単離

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Isolation of lignin-carbohydrate complexes. (IV). Application to red pine wood

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Abstract: Ozonation followed by acid hydrolysis was applied to red pine wood meal to isolate the benzylic ether type lignin-carbohydrate bonds (LCC bonds). The yield of the acidic fraction which contained LCC products was increased by extending ozonation and using weak anion exchange resin for anion exchange chromatography. There were many products in the acidic fraction with similar retention time on GC chromatogram after trimethylsilylation. Therefore, the identification of the products was difficult. It was improved by applying acetylation instead of trimethylsilylation. Some peaks on GC chromatogram of the samples from red pine wood showed the same retention time and the similar mass fragment pattern compared with the authentic compounds from LCC model compounds. These results suggested that benzylic ether type LCC bonds existed in red pine wood.

2004-P03

ケナフの成熟段階と部位の違いによる化学成分の変化

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Difference of chemical components of *Hibiscus cannabinus* bast and core between various maturation steps

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Abstract: *Hibiscus cannabinus* plant grown in the Agricultural and Forestry Research Center at the University of Tsukuba were separated into three parts (up, middle and bottom), and their bast and core parts were subjected to lignin and carbohydrates analyses. The middle and bottom parts of the bast were treated under soda-anthraquinone pulping and totally chlorine-free bleaching conditions, and the results were compared with those from *Acacia mearnsii.*

2004-P04

SEC-UV-MALS 法を用いた針葉樹クラフトパルプの特性解析

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SEC-UV-MALS analysis of softwood kraft pulp

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Graduate School of Agricultural and Life Sciences, the University of Tokyo

Abstract: Various cellulose and pulp samples including softwood kraft pulp (SKP) were dissolved in 8% lithium chloride/1,3-dimethyI-2-imidazolidinone (LiCl/DMI) and 8% LiCl/N,N-dimethylacetamide (LiCl/DMAc), and the obtained solutions were analyzed by size-exclusion chromatography equipped with ultraviolet and multi-angle light scattering detectors (SEC-UV-MALS). The conformation analysis using 1% LiCI/DMI as an eluent revealed that some compact structures consisting of cellulose, hemicellulose and lignin are present in the high MM part of SKP/LiCl/DMI. This structure was not broken by bleaching or removal of lignin, while it was susceptible to acid treatments and β-1,4-mannanase treatments. Thus, glucomannan seems to be a key component of the structure.

2004-P05

分軸添加型ラボ蒸解装置を用いたキノン蒸解法の検討

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Studies on quinone cooking using laboratory cooking equipment applied to modified cooking processes

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Abstract: Quinone has been used as a cooking additive in many KP mills. This paper shows how quinone is applied to recent modified cooking processes. In order to make conditions of laboratory test similar to the ones of a real digester, we developed a small scale digester in which addition and extraction of cooking liquors are possible. Using this equipment, the following results became clear.

1. Addition of quinone at the top of digester is most effective. The effect of quinone is decreased if it is added after the start of cooking. 2. The amount of extracted SAG (solution-type quinone) from a digester accompanying the extraction of black liquor is very small. But the large amount of AQ (slurry-type quinone) is extracted under the lower concentration of active alkali.

2004-P06

摩砕によるリグニン構造の変化について

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Changes of lignin structures caused by milling

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Abstract: In this paper, we tried to investigate the effect of milling on the structural change of lignin under

various milling conditions. Milled woods prepared under different conditions were analyzed by ozonation method 4). Both the content of β-O-4 structure and the diastereomer ratio (*erythro / erythro* + *threo*) decreased with the progress of milling. It was found that lignin undergoes the same degree of structural change when woods were milled to the same extent regardless of the difference of milling condition.

2004-P07
リグニン構造論におけるオゾン分解法の最近の展開
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Recent contribution of ozonation method to structural analysis of lignin
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Abstract: Recent development of ozonation method and its contribution to lignin chemistry is reviewed. The presence of simple relationships between stereo structure of β-O-41inkage and aromatic ring type has been suggested. This relationship seems to be valid not only to woods but also to lower plant. Stereo preferential reactions of lignin during many kinds of chemical and mechanical treatments were detected by ozonation analysis.

2004-P08
腸内細菌に対するリグニンの影響
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Effect of lignin on the growth of enterobacteria
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Abstract: Several kinds of enterobacteria were cultured with the medium containing lignin that had been derived from rice bran. Lignin was metabolized by *Escherichia coli* and Staphylococcus epidermidis. In the medium with lignin, the growth of *Lactobacillus acidophilus* and *Streptococcus intermedius* was augmented. On the other hand, the growth of other enterobacteria such as *Escherichia coli* was supressed.

2004-P09
脱水素重合時におけるシンナミルアルコール類と 4-クロロアニリンとの反応
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Structural elucidation of chloroaniline-lignin matrix by pyrolysis-gas chromatography with on-line methylation
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Abstract: Agrochemicals containing organochlorine compounds remain in soil. These compounds are incorporated into lignin and humic acid. In order to clarify the fate of organochlorine compounds, bulk guaiacyl- and syringyl dehydrogenative polymers (DHPS) were prepared in the presence and absence of 4-chloroaniline, and analyzed with on-line methylation pyrolysis gas chromatography/ mass spectrometry using tetramethylammonium hydroxide (TMAH), TMAH-Py- GC/MS. In TMAH-Py-GC/MS of coniferyl alcohol-DHP incorporating chloroaniline, (4-chloro- phenyl)-[1-(3,4- dimethoxyphenyl)-2,3-dimethoxypropyl] amine was detected as a pyrolysis product; a similar syringyl product was obtained from TMAH-Py-GC/MS of sinapyl alcohol/chloro -aniline-DHP. In TMAH-Py-GC/MS of DHPs incorporating chloroaniline, the amounts of β-O-4 substructure- derived products, *erythro/threo*-1-(3,4-dimethoxyphenyl)-1,2,3-tri-methoxy- propane and 1-(3,4,5- trimethoxyphenyl)-1,2,3-trimethoxypropane, were greatly decreased compared to those from DHPs without chloroaniline. The pyrolysis results directly proved that the incorporation of 4-chloroaniline into the Cα-position of arylglycerol-β-guaiacyl ether substructures.

2004-P10
スギリグニンの熱分解における各種単位構造の役割
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Role of substructure in pyrolysis of Japanese cedar lignin
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Abstract: To elucidate the pyrolysis behavior of lignin in wood, pyrolysis behavior of milled wood lignin (MWL) isolated from Japanese cedar (*Cryptomeria japonica*) was studied at 200-400ºC in nitrogen. As a result, condensation preferentially occured at 200-300ºC rather than depolymerization, substantial depolymerization started at 300-350ºC, and carbonization started at 350-400Qc. Methylation of the OH groups stabilized the MWL sample for condensation as indicated by raising the condensation temperature by 50-100ºC, while the methylation did not change the reactivities of depolymerization and carbonization. With the results of dimeric model compounds, role of the substructure in lignin in these pyrolysis behaviors is also discussed. These results will give useful suggestions for controlling the product selectivity, low molecular weight substances vs. char, from lignin in wood.

2004-P11
リグノフエノールエポキシ樹脂の合成と物性
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Synthesis and properties of lignophenol/epoxy resins
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Abstract: Lignophenol/epoxy resins were prepared from lignophenols (LP), epoxy compounds (E), and triethylene tetramine. They were prepared at various weight ratios of LP and E, LP/E, and various molar ratios of N-H and epoxy group, [NH]/[Epoxy]. N,N-dimethylformamide (DMF) solubility and the viscoelastic properties of cured resins were investigated. The solubility of DMF increased with increasing LP/E ratios. The resins with LP/E=1/1 and [NH]/[Epoxy]=0.5 had the highest peak temperature of loss modulus. The breadth of the temperature-modulus curve in the transition region was estimated quantitatively according to the Kwei's equation which indicates the, steepness of the dispersion curve.

2004-P12
アカマツ硫酸リグニンのレゾルシノール化
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Resorcinolization of red pine sulfuric acid lignin
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Abstract: To enhance the reactivity and the solubility of sulfuric acid ligmin (SAL), treatments with resorcinol in the presence of 72% sulfuric acid catalyst were performed. When resorcinol concentration was sufficiently high, resorcinolized sulfuric acid lignin with higher solubility to organic solvent was obtained. Compared with phenolization of SAL, larger amount of acid soluble fraction of reaction product was yielded. But molecule weight of resorcinolized product was larger than that of phenolized one. This may be interpreted that decomposed SAL was re-polymerized during the resorcinolized reaction.

2004-P13
ヒラタケにおける多機能型ペルオキシダーゼ MnP2 組換え遺伝子の発現
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Expression of recombinant versatile peroxidase MnP2 in *Pleurotus ostreatus*
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Research Institute for Sustainable Humanosphere, Kyoto University

Abstract: *Pleurotus ostreatus* secrets an unique peroxidase, MnP2 predominantly in low nitrogen condition. MnP2 can oxidize not only Mn^{2+} but also non-phenolic and high-molecular weight compounds directly [1]. To express MnP2, we made expression plasmid containing the coding sequence of *mnp2* between *P. ostreatus sdi1* promoter and terminator sequences and introduced the plasmid to P. ostreatus. We isolated 33 transformants containing the recombinant *mnp2* sequence. Through screenings for elevated decolorizing activity of Poly R-478, one of the recombinants, TM2-10 was selected. On a synthetic medium containing 15 mM ammonium oxalate, specific expression of rMnP2 by TM2-10, but not wild-type control, was demonstrated with anion- exchange chromatography.

2004-P14

白色腐朽菌 *Ceriporiopsis subvermispora* の産生するジカルボン酸 ceriporic acid B アナログの合成と機能解析

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Synthesis and functional analysis of dicarboxylic acid, ceriporic acid B produced by a white rot fungus *Ceriporiopsis subvermispora*

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Abstract: Previously, we reported that 1-nonadecene-2, 3-dicarboxylic acid (ceriporic acid B, NDA) inhibited production of •OH by the Fenton reaction. The present research aimed at elucidating effects of the alkyl side chain of this metabolite on iron redox reactions and the Fenton reaction. To discuss on the structure-function relationship, we synthesized 1-undecene-2, 3-dicaroboxylic acid (UDA), an analogue of ceriporic acid B. Using UDA, NDA and itaconic acid, we analyzed surfactant activities, suppression of Fe^{3+} redox reaction and inhibition of •OH production. As a result, we found that UDA suppressed •OH production by the Fenton reaction less effectively than NDA. No inhibitory effects were found for itacomic acid. These results indicate that chain length of the alkyl side chain is a key factor for controlling iron redox reactions and inhibition of •OH production by the Fenton reaction.

2004-P15

担子菌カワラタケの遺伝子組換えによるラッカーゼの高生産

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Overproduction of recombinant laccase using a homologous expression system in *Coriolus versicolor*

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Abstract: One of the major extracellular enzymes of the white-rot fungus *Coriolus versicolor* is laccase, which is involved in the degradation of lignin. We constructed a homologous system for the expression of a gene for laccase III in *C. versicolor* using a chimeric laccase gene driven by the promoter of a gene for glyceraldehyde-3-phosphate dehydrogenase from this fungus. We transformed *C. versicolor* successfully by introducing both a gene for hygromycin B phosphotrans- ferase and the chimeric laccase gene. We examined one of the transformants that had the highest laccase activity and found that its activity was significantly higher than that of the wild type.

2004-P16

マンガンペルオキシダーゼによる変異原性物質の分解と無毒化

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Degradation and detoxification of mutagen by manganese peroxidase

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Abstract: 3-*Tert*-butyl-4-hydroxyanisole (BHA), which is a phenolic compound widely used as an antioxidant for foods and cosmetics, displays both mutagemic and estrogenic activities. Therefore, we investigated whether manganese peroxidase (MnP) can degrade and remove the mutagenic activity. BHA completely disappeared in the reaction mixture after a 24-h treatment with MnP, and the mutagenic activity of BHA was also completely removed. These results indicate that the MnP is effective in degradation and detoxification of BHA. The GC-MS analyses indicated that the major metabolite of BHA is 2,2'-dihydroxy-5,5'-dimethoxy-3,3'-di-*tart*-butylbiphenyl (M1).

2004-P17

白色腐朽担子菌による塩素化ダイオキシン類の分解特異性

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Specificity for the degradation of polychlorinated dioxins by white-rot fungi

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Abstract: The model compounds of polychlorinated dibenzo-*p*-dioxins (PCDDs), 2,7-dichloro-, 2,3,7-trichloro, 1,2,6,7-, I,2,8,9-, 1,3,6,8-tetrachlorodibenzo-*p*-dioxin and the model compounds of polychlorinated dibenzofuran, 2,8-dichloro, 2,4,8-trichlorodibenzofuran were used as substrate for degradation experiment by white-rot fungi *Phlebia lindtneri,* and *Phlebia brevispora*. In the cultures treated with *P. lindtneri*, the degradation rate of 1,2,6,7-tetraCDD was higher than that of 2,3,7- triCDD, and no degradation of 1,3,6,8-tetraCDD was observed. These results indicate that the degradation of PCDDs depend more strongly chlorinated position than the number of chlorinated substituents. Degradation rate of polychlorinated dibenzofuran was lower than that of polychlorinated dibenzo-*p*-dioxin. On the other hand, 1,3,6,8-tetrachlorodibenzo-*p*-dioxin, 2,8- dichloro, and 2,4,8-trichlorodibenzofuran were degraded by *P. brevispora*. Monohydroxylated and monomethoxylated compounds were detected as metabolite from the cultures treated with *P. brevispora.*

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2005-101

マツ木部組織における過ヨウ素酸リグニンの ToF-SIMS 測定

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Investigation of periodate lignin from *Pinus thunbergii* xylem using ToF-SIMS

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Abstract: Periodate lignin structures of the differentiating xylem of normal and compression wood of pine were investigated using time-of-fright secondary ion mass spectrometry (ToF-SIMS). In a previous study, the morphological features of lignin have shown to be retained after the removal of polysaccharides by periodate oxidation. Xylem tissue samples were pre-methylated with CH_2N_2 to protect free-phenolic groups in lignin from undesirable oxidative modification, and then were treated with periodate. The spectra of compression wood treated with periodate showed both the ions derived from units having free-phenolic groups and the ions derived from lignin units having a methylated phenolic hydroxyl group at m/z 165 for guaiacyl and at m/z 135 for *p*-hydroxyphenyl units. Comparison of the ToF-SIMS spectra of untreated, CH_2N_2-treated, and CH_2N_2-periodate- treated samples gave a good explanation for the behavior of periodate oxidation observed in intact xylem tissues of wood.

2005-102

^{13}C 標識テトラメチルアンモニウムヒドロキシドを用いた熱分解—メチル化によるリグニンの分析

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^{13}C-Labeled tetramethylammonium hydroxide (TMAH) thermochemolysis of lignin

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Abstract: A bulk dehydrogenation polymer of coniferyl alcohol (G-DHP) and a Japanese ceder wood were methylated with diazomethane and subjected to ^{13}C-labeled tetramethylammonium hydroxide (13C-TMAH) thermochemolysis (315ºC/4s). Products having diazomethane- and analytically-added methyl groups were transferred to GC/MS. MS data of the products showed that (1) veratrylaldehyde (**2**), β,3,4-trimethoxystyrene (**5**) extensively stemmed from nonphenolic β-aryl ether subunits, and 1-(3 ,4-dimethoxyphenyl)-1,2,3-trimethoxypropane (**7**) stemmed from both phenolic and nonphenolic β-aryl ether subunits, (2) the DHP had phenolic guaiacylglycerol moieties involved in β-aryl ether linkages in a larger abundance than nonphenolic ones, in contrast to the wood lignin, (3) coniferyl alcohol dimethyl ether (**6**) observed in the DHP pyrogram stemmed from 4-*O*-etherified coniferyl alcohol and **6** produced from the wood stemmed from both 4-*O*- and Cγ-*O*-etherified corliferyl alcohols in roughly equal amounts, (4) pinoresinol dimethyl ether (**11**) showed the M^+ ions both at *m/z* 387 and *m/z* 388 in a roughly 1:2 signal intensity ratio, suggesting that 1/3 β-β subunits are present at the terminal of the DHP network, and (4) stilbenes **8-10** showed the molecular ion at m/z 373, suggesting that these stem from terminal β-5 subunits.

2005-103

酸性条件下におけるリグニン β-O-4 結合解裂機構の再評価（1）

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Reinvestigation of the mechanism of lignin β-O-4 bond cleavage under acidic conditions (1) -Experiments using C_6-C_2 model compounds

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Abstract: Acidolysis of lignin containing materials has widely been applied as a method for isolation as well as structural analysis of lignin. The most important chemical reaction in these methods is the cleavage of β-O-4 bond in lignin. Although the mechanism of the cleavage has been postulated, it seems not to be rationale when the known phenomenon, the rate of the cleavage is dependent on the concentration and kind

of acid, is taken into consideration. The objective of this research is to propose a more rationale mechanism for the cleavage of lignin β-O-4 bond in acidolysis and to examine its kinetic in detail. To avoid complexities of the reaction caused by the presence of γ-hydroxymethyl group, a C_6-C_2 model compound was used in this paper. The model was subjected to an acidolysis under various conditions and its degradation and kinetic were thoroughly examined.

2005-104

モノリグノール配糖体の HRP 触媒脱水素重合

飛松裕基、上高原浩、高野俊幸、中坪文明
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HRP catalyzed dehydrogenative polymerization of monolignol glucosides

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Abstract: High yields synthesis of (*E*)-isoconiferin, (*E*)-triandrin and (*E*)-isosyringin, which had a hydrophilic D-glucose unit on their γ positions of the respective monolignols, were established and their HRP catalyzed polymerizations in homogeneous systems were conducted. Under optimum conditions, isoconiferin and triandrin gave polymers with DPn = 42-47 in high yields,
while the DPn of conventional DHPs were around 10. But the polymerization of isosyringin gave
a polymer in ony 28% yield and the DPn of the polymer was in the same range with that of DHP from sinapyl alcohol. The copolymerization of isosyringin and isoconiferin, however, gave a copolymer with DPn = 27 in 80% yield.

2005-105

形質転換樹木リグニンの迅速分析 −透過型近赤外分光法の応用−

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Rapid analysis of transgenic tree lignin, Application of transmittance near infrared spectroscopy

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Abstract: Our extensive functional genomic research on lignin biosynthesis has produced highly improved transgenic trees. To efficiently monitor and control the properties of the transgenic products a rapid mini scale analytical method is required. Transmittance near infrared (NIR) spectroscopy was chosen as a rapid lignin analysis tool. Pellets were prepared from 75 mg of wood meal and directly scanned. Very strong correlations were obtained between the conventional wet chemistry results and the NIR data for lignin content and S/G ratio. The results indicate that transmittance NIR is a powerful tool for determining and screening the chemical properties of transgenic trees.

2005-106

酸素処理過程におけるリグニン構造変化の赤外分光法による解析（4）−酸素処理に抵抗性を示すフェノール類の生成について−

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Infrared study of structural changes of lignin during oxygen treatment : part 4. Generation of resistant phenolic structure to oxygen treatment

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Abstract: For the fundamental study of oxygen delignification of kraft pulp, structural changes of kraft lignin during alkaline oxygen treatment was studied. At the early phase of the treatment, not only the generation of muconate substructure but the generation of some resistant phenolic substructures toward the treatment were suggested from the measurement of UV-VIS spectra at various pH. Furthermore formation of carbonyl groups was indicated by the time series analysis of infrared ATR spectra. Correlation analysis between this carbonyl band and other infrared bands under pH perturbation indicated that a part of carbonyl groups should be conjugated with phenolic substructure. In addition, the time series analysis of ^{1}H-NMR indicated that changes of the structural circumstance of a methoxyl group were occurred by the modification of a side chain part of lignin structure. These three results could be explained by the generation of a phenolic substructure conjugated with a carbonyl group, and *o*-vanillin type phenolic structure formed by the olefinic side chain cleavage of *o*-*p*-stilbene moiety can be a possible structure. Here, a stilbene structure should be generated from a phenolic phenylcoumaran moiety as the result of kraft cooking.

2005-107

美唄泥炭湿地からの水溶性有機物の分析

勝亦京子、Zhenfu Jin、堀啓映子、飯山賢治
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Chemical feature of dissolved organic matter from Bibai swamp

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Abstract: Water passed through peat swamp colored in brown to dark brown by dissolving organic matters (DOM). When the DOM in water now in ocean, such DOM could form chelates with metal ions in ocean water. The chelates would be insoluble in ocean water, and accumulate at the ocean bed as sediments. Lignin, which is significantly resist to biological decomposition, is the major component of DOM, has high ability of chelate formation. The behavior of water-soluble lignin is significantly important factor for global carbon circulation, but quite limited information is available. We started to investigate to make clear chemical structure of water-soluble lignin under natural condition and reaction under global system. The DOM was isolated from water at Bibai peat swamp in Hokkaido, the chemical feature of the DOM was analysed using some wet and spectrometric analyses. The major component of DOM would be highly modified lignin by activities of microorganisms.

2005-108

Characteristics of bast and core lignins of kenaf (*Hibiscus cannabinus*) and mulberry (*Morus bombycis*)

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Abstract: Structural characteristics of bark and core lignins from kenaf (*Hibiscus cannabinus*), paper mulberry (*Broussonetia kazinoki*) and mulberry (*Morus bombycis*) were examined. All of bark fractions gave lower Klason lignin contents than those of core fractions. Kenaf bark exhibited significantly high S/V molar ratio. High ratio of *elythro*- to *threo*-form (E/T ratio) of β-O-4 structure in lignin o kenaf bark was confirmed by both ozonation and ^{1}H-NMR analysis. Lignin structure of kenaf bark was comparable to core lignin while paper mulberry and mulberry bark exhibited quite different lignin characteristics comparing to core lignin.

2005-109

Feasibility of branch of young *Acacia mangium* Willd as raw material for pulp and paper manufacture

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Abstract: To examine the feasibility of branch of *Acacia mangium* with diameter less than 8 cm as a raw material for pulp production, we carried out a systematic fundamental study. Those branches are usually left on the ground as logging wastes in a plantation. Based on their chemical composition and fiber dimensions, we concluded that the quality of branches of *A. mangium* is as good as its trunks as raw materials for pulp and paper production. It was also suggested that yield and qualities of pulps might not be spoiled significantly even if branches with bark are subjected to pulping with trunks.

2005-110

Ozone bleaching for the low-kappa- number kraft pulp of wheat straw

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Abstract: This study has investigated the ozone bleaching for low-kappa-number kraft pulp of wheat straw, and the low-kappa- number kraft pulp was produced by the one stage extended delignification technology. Results showed 86.9% (SBD) brightness of bleached pulp could be achieved and the viscosity of the pulp could be S51ml/g after the AZEYP bleaching sequences. Lignin is the natural protector to carbohydrate. The Ozone delignification is important and benefit for TCF bleaching.

2005-111

Synthesis and properties of cationic lignin surfactant
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Abstract: Cationic lignin surfactant was synthesized by reacting kraft lignin with quaternary ammonium salt cationic 3-chloro-2-hydroxypropyl-trimethylammonium chloride (CHPTMAC). The effects of CHPTMAC dosage, NaOH dosage, reaction temperature and reaction time on the surface activity, nitrogen content and solubility of cationic lignin surfactants were studied. The results indicated the suitable synthesis conditions of cationic lignin surfactant were as follows: the dosage of quaternary ammonium salt (CHPTMAC) was 4 mol/kg lignin, the molar ratio of NaOH to quaternary ammonium salt agent was 1.3, reaction temperature was 50ºC and reaction time was 4 h. Synthesized cationic lignin surfactant had good solubility under different pH value, the highest nitrogen content was 2.57% and the lowest surface tension of them was reached 42.7 mN/m.

Keywords: kraft lignin, quaternary ammonium salt, cationic lignin surfactant, nitrogen content, surfactivity.

2005-112
リグニンを含有するヒドロキシプロピルセルロースゲルの熱的性質とゲスト分子との相互作用
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Thermal property of hydroxypropylcellulose bearing lignin gel and its interaction with guest molecules
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Abstract: Hydroxypropylcellulose bearing lignin (HPC-L) was prepared from unbleached acetic acid pulp of Todo-fir. The pulp derivative was converted to hydrogel with ethyleneglycol diglycidyl- ether as a crosslinker. The resultant gel showed exothermic peak in differential scanning calorimetry, of which temperature was consistent with that of gel shrinking. The temperature was elevated by adsorption of ionized dye. Thus, the thermal property was altered by the interaction with guest molecules. In addition, the gel showed different swelling behaviors upon interaction with ionic and nonionic surfactants.

2005-113
HBS パルプ化の実証試験―リグニン利用の可能性―
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Verification test of HBS-pulping: Possibility of lignin utilization
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Abstract: Y. Sano et al. developed the HBS-pulping method that could operate even on a small scale at a native locality of woody biomass. We undertook a verification test of this method including HBS pulping of softwood and agricultural husks, preparation of monosaccharide by pre-hydrolysis, enzymatic saccharization of HBS pulp, quality of silica contained in agricultural husks, preparation of fiberboard, appliation of HBS lignin to medical field, feasibility study and conceptual design of HBS- pulping process. In this symposium, we report the results of the verification test of HBS pulping from the point of view of lignin utilization.

2005-114
酢酸リグニン/合成ポリマー複合体の調製と分子間相互作用の評価
寺本好邦、田中紀子、遠藤貴士
産業技術総合研究所

Preparation and characterization of intermolecular interaction of organosolv lignin, acetate / synthetic polymer composites
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Abstract: Binary blends and pseudo complexes of organosolv lignin, acetate (OSL-Ac) with poly(*N*-vinyl pyrrolidone) were prepared, respectively, by casting from mixed polymer solution in *N,N*-dimethylformaide as good solvent and by spontaneous co-precipitation from solutions in tetrahydrofuran as comparatively poor solvent. Fourier transform inbred meastwements revealed the presence of rather stronger hydrogen-bonding interactions between hydroxyls of OSL-Ac and carbonyls of *N*-vinyl pyrrolidone units for the complexes than those for the blends. Thermal transition data obtained by

differential scanning calorimetory suggested that the blends are miscible,
whereas, for the complexes, a high frequency of interactions combined OSL-Ac with PVP intimately in the complexes to reduce the mobilities of the individual polymer chains.

2005-115

リグニンベースのポリイオンコンプレックスの調製と機能開拓

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Preparation and functionalization of lignin-based poly-ion complex

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Abstract: Poly-ion complexes of anionic lignosulfonic acid (LSA) with cationic poly(2-vinyl pyridine) or poly(4-vinyl pyridine) were prepared by spontaneous precipitation from solutions in dimethyl sulfoxide or diluted hydrochloric acid. Fourier transform infrared measurenent8 for the complexes revealed the presence of strong ionic interactions between sulfonic anion of LSA and pyridimium cation of vinylpyridine (VPy) polymer. The emergence of the strong interaction was supported by striking elevation of glass transition temperature in differential scanning calorimetry
measurements. Subsequently, thin-layered coating of lignin on VPy polymer films was conducted successfully to vary their surface property, as evidenced through visualization of the LSA component by atomic force microscopy.

2005-116

リグニンベース木質粒子分散型ポリウレタン複合体パネルの調製と物性

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[*1] 福井工業大学工学部、[*2] 産業技術総合研究所、[*3] リグノセルリサーチ

Preparation and mechanical properties of wood panel with lignin-based polyurethane composites

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Abstract: Wood panels with kraft lignin (KL)-based polyurethane (PU) compsites were prepared using three kinds of ethylene glycols, such as diethylene glycol, triethylene glycol or polyethylene glycol. Wood powder and coffee residue were used as fillers. Filler content (=filler/polyol, g/g) in KL polyol was varied from 50 to 100 %. Apparent density and mechanical properties of wood panels with the above PU composites were investigated as functions of filler contents and molecular mass of ethylene glycol. Flexural strength calibrated with apparent density was correlated with filler content. For the panel with PU composites filled with wood powder, the optimum point was observed at around filler content 70 to 80 %. Modulus of elasticity ranged from 3 to 6 GPa, suggested that panels obtained in this study are sufficiently strong for practical applications.

2005-特別講演

リグニン化学構造の不均一性

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Structural heterogeneity of lignin

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Abstract: Structural heterogeneity seems to be a key to understand the real structure of lignin and to discuss how lignin is deposited in the course of cell wall formation. Structure of lignin is believed to be not homogeneous in wood, but to be different dependent on the tissues of wood fiber, vessel and ray cell, on the cell wall layers of middle lamella, primary wall and secondary wall, and even in a lignin molecule. In order to characterize a lignin in a particular layer of cell wall, the fractionation of disintegrated wood and the separation of differentiating xylem were introduced. By these methods, structural characteristics of lignin in the compound middle lamella were obtained. It is well known that Milled Wood Lignin (MWL) does not represent whole lignin in wood but is originated from the compound middle lamella at least in the case of hardwood MWL obtained at the early stage of milling. Ozonation is truly epoc-making for the structural analysis of lignin, by

which stereostructural characteristics of lignin side chain part were obtained, and β-O-4 structure in lignin was for the first tine confirmed to be in a racemic form and optically inactive. It is also important to note that syringaldehyde ratio by alkaline nitrobenzene oxidation and erythronic acid ratio by ozonation are in a linear relationship. Development of new and controlled degradation methods and advanced microscopic technologies may open a new stage for the study of the structural heterogeneity of lignin.

2005-201

イネをモデルとした植物細胞壁形成過程に関する研究　－糖代謝系とシキミ酸経路、フェニルプロパノイド経路との共役、及びその遺伝子発現制御機構－

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Study for the process of cell wall formation in rice plant. - Conjugation and regulation of gene expressions among three metabolic pathways, carbohydrate metabolism, shikimate pathway and phenylpropanoid pathway

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Abstract: Plant cell walls contain polysaccharides-linked hydroxycinnamoyl ethers (PHEs) which consist of the ester-linkages between hydroxycinnamic acid derivatives such as ferulic acid (PA), *p*-coumaric acid (*p*CA) and cell wall matrix polysaccharides. Those hydroxycinnamic acids, in the Gramineae, mainly compose the ester linkages mainly with arabinoxylan or slightly with xyloglucan. They also compose ether-linkages with cell wall lignin units to form covalent ester-ether bridges between polysaccharides and lignins. A novel rice dwarf mutant Fukei 71 is found ectopically accumulating PHEs in the cell walls of internode pith parenchyma. We have pursued molecular and genetic analyses with Fukei 71 in order to clear PHEs biosynthesis in rice.

2005-202

イネをモデルとした植物細胞壁形成過程に関する研究 -Glycosylphosphatidylinositol-anchored protein はイネの細胞壁高次構造形成にどのように関わるのか？

鈴木瑠[*1]、武内佐知[*1]、佐藤かんな[*1]、半智史[*2]、北野英己[*3]、船田良[*2]、梶田真也[*1]、片山義博[*1]

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Study of plant cell wall formation in *Oryza sativa* L. -How does glycosylphosphatidylinositol -anchored protein relate to cell wall conformation in rice plant (*Oryza saliva* L.)

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Abstract: The advances in microscopy, molecular biology and genomics converged to make work easier for biologists to study the mechanism and process of cell wall conformation. Many biologists used *Arabidopsis thatiana* as a model plant to study cell wall conformation, and they revealed there are many genes involved in plant cell wall conformation. But few knowledge came out about detailed mechanism and process of wall formation. In this study, we used brittle culm mutant called cwa1, recessive mutant rice plant (*Oryza sativa* L.), to obtain new information about plant cell wall conformation which are not revealed in Arabidopsis study.

2005-203

ゴマの機能性リグナン，特にセサミノールの生合成について

片山健至[*1]、小堀里恵[*1]、鈴木利貞[*1]、並木満夫[*2]、田代亨[*3]

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Biosynthesis of functional lignans, particularly sesaminol, in *Sesamum indicum* seeds

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Abstract: To clarify biosynthesis of sesaminol, one of the strongest antioxidant lignans in sesame seeds, feeding experiments of L-[U-^{14}C]phenylalanine (Phe) were carried out. A solution of L-[U-^{14}C]Phe (10mM, 20□l) was injected into unripe capsules of 11 week-old (after seeding) intact *Sesamum indicum* plants cultivated in pots and then the plants were cultivated for a week at 26°C. The order of the percent incorporation of the radioactivity into the sesame lignans is as follows: sesamin > sesamolin > sesaminol ≥ pinoresinol > 7-episesaminol. It was found for the first time that the radioactivity was clearly incorporated into free sesaminol and 7-episesaminol in the seeds in a 100 : 8-9 ratio, but not into those in the pods. The percent incorporation into sesamin, sesamolin, and (+)-pinoresinol, in the seeds was 5-38 times larger than that in the pods.

2005-204

MROMT に相同性の高い新規フラボノイド OMT について

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A novel flavonoid *O*-methyltransferase having a high sequence similarity to MROMT

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Abstract: *Carthamus tinctorius* maturing seeds produce various secondary metabolites such as lignans, lignin, flavonoids, and serotonin amides of cinnamates. Recently, Umezawa et al. reported the cloning of the novel gene encoding lignan *O*-methyltransferase (matairesinol *O*-methyltransferase, *CtMROMT*) using *C.tinctorius* maturing seeds. In addition, they cloned a cDNA which shows a high sequence similarity to *CtMROMT* named *CtMROMTlike*. The present study identified the function of *CtMROMTlike*. Thus, the recombinant *CtMROMTlike*, expressed in *E. coli,* did not catalyze *O*-methylation of matairesinol, but catalyzed *O*-methylation of a flavonoid, apigenin, indicating clearly that *CtMROMTlike* was flavonoid *O*-methyltransferase (FOMT), but not MROMT.

2005-205

Arabidopsis thaliana の細胞分裂機構を用いた樹木資源の生産制御に関する研究

松井紀子[*1]、武内 佐知[*1]、西窪伸之[*1*2]、半智史[*3]、船田良[*3]、梶田真也[*1]、片山義博[*1]
[*1] 東京農工大学大学院 BASE、[*2]理化学研究所植物科学研究センター、[*3]農工大院農学教育部、Research on production control of woody resources with cell division mechanisms of *Arabidopsis thatiana*

Noriko Matsui, Sachi Takenouchi, Nobuyuki Nishikubo, Satoshi Nakaba, Ryo Funada, Shinya Kajita, Yoshihiro Katayama
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Abstract: The mechanisms by which plants modulate their growth rate in response to environmental and developmental conditions are unknown, but are presumed to involve specialized regions meristems where cells division is concentrated. In plant, as in other eukaryotes, the cell cycle consists of four different phases-G1(gap1),S(DNA synthesis), G2(gap2),and M(mitosis) phases.

The G1/S transition generally represents the principal point of commitment to cell division. Many of the components of the cell cycle core machinery regulating the G1/S transition in plant have been recently identified. In this study, we examined regulation cell division in vascular cambium with G1/S related genes, AtE2F, AtDP, AtCycD.

2005-206

植物ペルオキシダーゼの生理機能解明に向けたプロテオミクス

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Proteomic studies for physiological function of plant peroxidases

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Abstract: Higher plants possess a large set of the classical plant peroxidases. These peroxidases are

thought to participate in a wide rage of physiological functions. However, the most of them have been unclear. Using proteomic analysis, we surveyed the localization of plant peroxidase in various organs in *Populus alba* L. Peroxidase isoenzymes were extracted from the various organs and fractionated by a Concanavallin A Sepharose column. Approximately 20 protein spots were detected by the two-dimensional electrophoresis gels. Some anionic peroxidase isoenzymes were identified via the PMF analysis. One of the anionic peroxidases would be xylem and inner bark specific peroxidase.

2005-207
Phanerochaete crassa WD1694 の菌体外スライムと菌体外ペルオキシダーゼ活性染色について
高野麻理子、林 徳子
森林総合研究所
Slime of *Phanerochaete crassa* WD 1694 and its relationship to extracellular peroxidase activity staining
Mariko Takano, Noriko Hayashi
Forestry and Forest Products Research Institute

Abstract: Distribution of slime of the white-rot fungi *Phanerochaete crassa* WD1694 was studied by a microscope with phloxine B coloration and phase contrast technique. The slime was occurred inside of each mycelial pellets grown in the shaken culture containing unbleached kraft pulp. Hyphal tips that caused extracellular peroxidase staining did not had slime around the hyphae. Besides the strong coloration of extracellular peroxidase staining at the hyphal tips and on the hyphae protruding from mycelial pellets, the staining also occurred on the hyphae inside of the mycelial pellets and in slime among the hyphae. The results suggested that the localization of extracellular peroxidase staining on the mycelium was mainly due to the generation of oxidant at the hyphal tips and on the hyphae, and was also caused by fungal slime that might keep the generated oxodants.

2005-208
MnP による異常プリオンタンパク β−シート構造の分解
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Degradation of β-sheet structure of protease-resistant prion protein by MnP
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Abstract: Protease Resistant Prion Protein (PrP^{Res}) is a causual substance of bovine spongiform encephalopathy (BSE) and other prion diseases. PrP^{Res} has a high content of β-sheet structure, and can not be degraded either by proteases or usual chemical treatments. Thus, convincing method for the decontamination of PrP^{Res} is urgently required. We reported that PrP^{Res} was completely degraded by 8 white-rot fungi and it's crude extracellular enzyme. In this study, we assessed the PrP^{Res} infectious after the treatment by white-rot fungi. When PrP^{Res} was treated with *Ceriporia lacerata* MZ-340, intracerebral bioassay showed virtually no infectivity. In addition, keratin that has a high content of β-sheet structure as well as PrP^{Res} was also completely degraded by purified MnP from *C. lacerata* MZ-340. These results support that MnP produced by *C. lacerata* MZ-340 can degrade β-sheet structure.

2005-209
土壌浄化を指向した白色腐朽菌のスクリーニング
天野智絵、平井浩文、河合真吾、西田友昭
静岡大学農学部
Screening of white rot fungi aiming for soil remediation
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Faculty of Agriculture, Shizuoka University

Abstract: White rot fungus, tentatively named AG-200, which extensively degrades white birch (*Betula platyphylla* var japonica) wood-lignin was isolated by using hardwood kraft pulp and agar medium containing guaiacol. The partial sequencing data of 18S ribosomal DNA and the shape of fruit body suggested that the fungus AG-200 belongs to *Amauroderma* sp.. Great interest is currently being expressed in white rot fungi and their ligninolytic enzymes due to recognized potential for degrading and detoxifying recalcitrant environmental

pollutants such as dioxins. For practical application of white rot fungus to soil remediation, it is important that the fungus is resistant to contamination by autochthonous microorganisms in soil. Thus, we investigated whether AG-200 can degrade wood-lignin under highly acidic condition (pH 2.5) in which the grow of autochthonous microorganisms such as bacteria is inhibited. AG-200 had over 50% Klason lignin loss for 4 weeks of incubation under acidic and natural (pH 6) conditions, while the ligninolytic activities of *Phanerochaete sordida* YK-624 and IZU-154 were influenced by pH and markedly decreased under acidic condition. Therefore, it might be possible to use the acid-resistant fungus AG-200 for bioremediation of soil contaminated with aromatic compounds. Practical application of AG-200 to soil remediation should be the subject of a forthcoming study.

2005-210

リグニン分解酵素による4-tert-オクチルフェノールのエストロゲン様活性除去

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静岡大学農学部

Removal of estrogenic activity of 4-*tert*-octylphenol by ligninolytic enzymes

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Faculty of Agriculture, Shizuoka Universityan

Abstract: 4-*tert*-Octylphenol (4-TOP) is widely used in a variety of industrial and residential applications, and is suspected of having estrogenic (endocrine-disrupting) activity. Thus, 4-TOP was treated with the white rot fungi, *Phanerochaete sordida* YK-624 and *Trametes versicolor*, under ligninolytic condition with low-nitrogen and high-carbon culture medium. 4-TOP decreased by over 90% within 6 days of treatments with the two fungi and the activities of ligninolytic enzymes, manganese peroxidase (MnP) and laccase, were detected during treatment, which suggested that the disappearance of 4-TOP is related to ligninolytic enzymes produced extracellularly by white rot fungi. Therefore, 4-TOP was treated with MnP and laccase prepared from the culture of white rot fungi. Using the yeast two-hybrid assay system, it was confirmed that both enzymatic treatments completely removed the estrogenic activity of 4-TOP after 2 h. This result strongly suggests that ligninolytic enzymes are effective in removing the estrogenic activity of 4-TOP.

2005-211

白色腐朽菌 *Phlebia brevispora* による PCB の代謝変換

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Fungal metabolism of polychlorinated biphenyls by white rot fungus *Phlebia brevispora*

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Abstract: The degradation of individual PCB congeners in the culture of *Phanerochaete sordida*, *Phlebia acerina*, and *Phlebia brevispora* are examined. These fungi showed the different traits of degradation of each compounds. *P. sordida* showed any degradation of tested PCBs. *P. acerina* showed the degradation of 3,3',4,4'-tetraCB, although more chlorinated PCBs were not degraded. On the other hand, in addition to 3,3',4,4'-tetraCB (#77), 2,3,3',4,4'-pentaCB (#105), 2,3',4,4',5-pentaCB (#118), 3,3',4,4',5-pentaCB (#126), and 2,3',4,4',5,5'-hexaCB (#167) were degraded by *P. brevispora.* By GC/MS analysis, methoxylated and dechlorinated metabolites were detected from the culture with these compounds. This is the first report on the biotransformation of toxic coplanar PCBs by fungal strains.

2005-212

木材腐朽菌による PVA フィルムの分解

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Biodegradation of PVA film by wood-rotting fungi

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Abstract: A polyvinyl alcohol (PVA) film is used for the packing for food and fats, because it is indissoluble in water. Degradation efficiency of solid polymer is important in the viewpoint of material recycle. The screening of wood-rotting fungi for the biodegradation of PVA film was examined. Although no white-rot fungi degraded PVA film, one fungus in *Gloeophyllum* genus, *G. trabeum* degraded PVA film extensively. The clarification of the degradation mechanism of PVA film by this fungus is now on progress.

2005-213
白色腐朽菌から抽出した酵素による Polychlorinated biphenyls (PCBs) 分解の試み
松尾保洋、藤井啓太、伊藤和貴、橘燦郎
愛媛大学農学部
Study on degradation of polychlorinated biphenyls with an enzymes from white rot fungi
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Faculty of Agriculture, Ehime University

Abstract: Degradation of 3,3',4,4'-Tetrachlorobiphenyl (TCB) with crude enzymes from PL1 and the enzymes isolated from the crude enzymes was investigated_ About 40% of TCB was degraded by the crude enzynes in 48 hours in a liquid medium. Manganese peoxidase (MnP), Lignin peroxidase, Laccase and 1,2-Dioxygenase were isolated from the crude ezymes by ion-exchange and gel filtration chromatography. By the degradation of TCB with the isolated MnP in the liquid medium, about 7% of TCB was degraded in 24 hours. On the contrary, about 2% of TCB was degraded when the degradation of TCB with the immobilized MnP was conducted for 24 hours in the liquid medium. From the results obtained here, it is suggested that MnP in the crude enzymes might not play an important role on the initial stage of degradation of TCB. Furthermore, a degradation pathway of TCB with the crude enzymes was proposed by confirmation of the intermediates.

2005 パネルディスカッション「リグニン研究の過去・現在・未来」
パネリスト:京都大学名誉教授 越島哲夫、名古屋大学名誉教授 寺島典二、京都大学名誉教授 樋口隆昌、北海道大学大学院農学研究科 浦木康光、九州大学大学院農学研究院 堤祐司、 東京大学大学院農学生命科学研究科 横山朝哉
コーディネーター:名古屋大学大学院生命農学研究科 福島和彦

2005-P01
爆砕発酵処理バガスの抗酸化能と抗酸化性物質
大原誠資[*1]、橋田光[*1]、柏木豊[*2]、藤野哲也[*3]、稲福直[*3]、稲福盛雄[*3]
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Antioxidant activity of steam-exploded, fermented bagasse and related antioxidant substances
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Abstract: We have been studying for utilization of bagasse as foodstuffs. In this study, it has been found that steam explosion of bagasse followed by fermentation is an effective pretreatment not only on the formation of xylooligosaccharides, but also on increase in antioxidant activity. In addition, we examined steam explosion products of bagasse to elucidate the reaction mechanism causing the improvement of antioxidant activity. We concluded the following. 1) Antioxidant activity of steam- exploded bagasse is attributed to low molecular weight polyphenols formed during steam explosion. 2) Ferulic acid shows high antioxidant activity, while *p*-hydroxycinnamic acid and *p*-hydroxybenzoic acid don't. Ferulic acid is regarded as one of the compounds responsible for antioxidant activity of steam-exploded bagasse.

2005-P02
ニセアカシアのシリンギルリグニン生合成経路の探索
植田幸恵[*1]、中坪朋文[*2]、梅澤俊明[*2]、堤祐司[*3]、近藤隆一郎[*3]
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Search of syringyl lignin biosynthesis in black locust (*Robinia pseudoacacia*)
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[*1]Graduate School of Boiresources and Bioenvironmental Sciences, Kyushu University, [*2]Research Institute for Sustainable Humanosphere, Kyoto University, [*3]Graduate School of Agriculture, Kyushu University

Abstract: It was reported that administered sinapate was incorporated into syringyl lignin of *Robinia pseudoacacia* and that 4CL isoenzyme in *Robinia* utilized sinapate unlike other plant 4CLs. These findings are indicative of an alternative route of syringyl lignin biosynthesis where sinapyl alcohol is biosynthesized passing through sinapate and sinapoyl CoA. We therefore examined 4CL, ALDH, F5H, and COMT enzyme reaction in lignifying xylem of *Robinia* to investigate the biosynthetic pathways of syringyl lignin in *Robinia*. All the enzymes possess a larger substrate preferences toward syringyl substrates compared to the enzymes in other plant species ever reported. This result is an evidence for the presence of biosynthetic route of syringyl lignin via sinapate.

2005-P03

MWL 抽出残さ木粉に存在するリグニンの性状

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Characteristics of lignin structures in MWL isolation residue (MWLR)

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Abstract: Beech (*Fagus crenata* Blume) milled woods were extracted with dioxane/water (96 : 4, v/v). The extracts were separated by centrifugation and the insoluble fraction was obtained as MWL isolation residue (MWLR). In this paper, the characterization of lignin in MWLR was tried out. The characteristics of lignin structures in MWLR were analyzed by the ozonation method and alkaline nitrobenzene oxidation method. The *erythro* and syringyl ratios of MWLRs were similar to or slightly higher than those of the corresponding milled woods and always higher than those of corresponding MWLs. These results and the lower *erythro* ratio of MWLR than the original wood meal indicated that lignin in MWLR was never free from structural changes during milling.

2005-P04

β-*O*-4 型人工リグニンポリマーの合成 (4) —モノマー合成ルートの短縮—

岸本崇生、浦木康光、生方信
北海道大学大学院農学研究科

Synthesis of β-*O*-4 type artificial lignin polymer (4) - Improved synthetic methods for monomer

Takao Kishimoto, Yasumitsu Uraki, Makoto Ubukata
Graduate School of Agriculture, Hokkaido University

Abstract: The β-*O*-4 structure is one of the most important substructures in lignin. The first polymeric lignin mimic composed of only β-*O*-4 structure (DPw = 19.5-30.6) has been synthesized in our laboratory. In this investigation the synthetic method for the monomer was improved, where the starting material was changed from vanillin to acetovanillone.

2005-P05

DHP 調製における因子の検討

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Effect of DHP preparation factors on the chemical structures

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[*1]Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University, [*2]Graduate School of Agriculture, Kyushu University, [*3]Institute of Agricultural and Forest Engineering, University of Tsukuba

Abstract: DHP is made from *p*-hydroxycinnamyl alcohol by enzymatic polymerization, and it is used as a model compound for natural lignin. However the reaction conditions (pH, substrate additive rate, enzyme activity and so on) depend on each work and few people reported reproductivity of DHP preparation about yield and linkages. In this study, bulk DHP is enzymatically prepared from coniferyl alcohol under various pH conditions, and the chemical structures were examined by nuclear magnetic resonance (^{13}C-NMR) and pyrolysis gas-chromatography (Py-GC/FID). DHP prepared under low pH condition has higher abundance of β-O-4 linkage, and that of α-O-4 linkage was lower.

2005-P06

表面プラズモン共鳴を用いたモノリグノール類とヘミセルロースの相互作用（III）

中村淳、浦木康光、岸本崇生、生方信
北海道大学大学院農学研究科

Investigation on interaction between monolignols and hemicelluloses using surface plasmon resonance (III)

Atsushi Nakamura, Yasumitsu Uraki, Takao Kishimoto, Makoto Ubukata
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Abstract: To clarify lignin biosynthesis, we investigated on the interactions of hemicelluloses (xylan and glucomannan) with monolignols (coniferyl alcohol and sinapyl alcohol) and its glucosides (coniferin and siryngin), and horseradish peroxidase by using surface plasmon resonance. The adsorption capacities of the oxidized hemicelluloses to monolignols were much larger than those to their glucosides. The interaction seems to be due to the hydrophobic interaction. The adsorption of HRP to xylan was likely to be specific, and its amount was larger than that to glucomannan. lt is suggested from these results that substrate of lignin biopolymerization is supplied as monolignols from cytoplasm, and polymerized in xylan matrix.

2005-P07

リグニン前駆物質と多糖の相互作用に関する研究

藤加珠子、湯口宜明
産業技術総合研究所

Study on interaction of lignin precursor substances and polysaccharide

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National Institute of Advanced Industrial Science and Technology

Abstract: Xyloglucan is a kind of hemicellulose, and exists in the cell wall or seed in the higher plants. We investigated that xyloglucan aqueous solution took place gelation by addition of precursors of lignin as coniferyl alcohol or sinapyl alcohol. Coniferyl alcohol needed for the formation of hydrogel was very low concentration of 0.75wt% with 0.5wt% xyloglucan at 5ºC. The change in the line shape of the ESR spectrum was also observed during the sol-gel transition of these mixtures.

2005-P08

白色腐朽菌 *Phanerochaete sordida* YK-624 株の産生する新規リグニンペルオキシダーゼによる塩素化芳香族化合物の分解

平井浩文、政氏恵理、高橋昭裕、河合真吾、西田友昭
静岡大学農学部

Degradation of polychlorinated aromatic compounds by novel lignin peroxidase from white-rot fungus *Phanerochaete sordida* YK-624

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Abstract: We tried to degrade various polychlorinated aromatic compounds by novel lignin peroxidase (YK-LiP) from *Phanerochaete sordida* YK-624. YK-LiP degraded 2,4,8-trichlorodibenzo- furan and 2,7-dichlorodibenzo-*p*-dioxin although LiP (Pc-LiP) from *P. chrysosporium* could not degrade these dioxins, and the degradation rate of methoxychlor by YK-LiP was greater than that by Pc-LiP. Moreover, YK-LiP degraded polychlorinated phenols more effectively than Pc-LiP. 2,4,6-Trichlorophenol (TCP) was converted to 2,6-dichloro-1,4-benzoquinone by YK-LiP. On the other hand, 2,6-dichloro-1,4-benzoquinone was not detected in MnP reaction mixture although the degradation of TCP by MnP was almost the same as that by YK-LiP.

2005-P09

白色腐朽菌から抽出した粗酵素によるダイオキシンの分解

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Biodegradation of dioxins with a crude enzyme from white-rot fungi

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Faculty of Agriculture, Ehime University

Abstract: To obtain the basic information for bioremediation of dioxin-contaminated soil by a crude enzyme from white-rot fungi, biodegradation of 2,4, 8-Trichlorodibenzofuran (2,4,8-TrCDF) was investigated.

By biodegradation of 2,4,8-TrCDF with a crude enzyme from fungus PL1 in a liquid medium, about 50% of 2,4,8-TrCDF was degraded in 72 hours. Furthermore, the enzyme degraded about 20% of 2,4,8-TrCDF in soil when the slurry phase biodegradation was conducted for 72 hours. These results suggest that bioremediation of dioxin-contaminated soil by a crude enzyme from white-rot fungi is possible.

2005-P10

白色腐朽担子菌の系統解析とダイオキシン分解性

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Phylogenic analysis and characterization of degrading dioxin for white-rot fungi

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Abstract: In our previous study, we found that some *Phlebia* genera species were capable of degrading 2, 7-dichlorodibenzo-*p*-dioxin (2,7-diCDD) as model dioxin compound. In the present paper, we focused on newly 42 *Phlebia* strains and screened them. As a result, only *Phlebia lindtneri* and *Phlebia acerina* could degrade 2,7-diCDD. In addition, most strains which belong to these three species were capable of degrading 2,7-diCDD. Therefore, we suggest that the ability of degrading chlorinated dioxin is conserved in the particular species of *Phlebia* genera.

2005-P11

白色腐朽菌による塩素系芳香族化合物の分解における 菌体内・菌体外酵素の役割について

丸吉美幸[*1]、亀井一郎[*1]、近藤隆一郎[*2]
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Roles of intracellular and extracellular enzymes in degradation of chlorinated aromatic compounds by white rot fungi

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Abstract: Various white rot fungi (*Phanerochaete, Phlebia, Pleurotus* and *Trametes* sp.) were used in degradation experiment of 4,4'-dichlorobiphenyl (4,4'-DCB), 2,7-dichlordibenzo-*p*-dioxin (2.7-DCDD), 1,3,6.8-tetraCDD and dichlorodiphenyltrichloroethane (DDT). Although DDT and 4.4'-DCB were degradated by most fungi, dioxins were effectively degradated by only *Phlebia* species, Decolorization of poly R 478 which was thought to involve with ligninolytic enzyme was compared with degradation of pollutants. Decolorization rate seemed to correlate with degradation of DDT, but not dioxins. Furthermore, piperonyl butoxide (inhibitor of cytochrome P450) inhibited degradation of 2,7-DCDD, but not DDT. These results indicate that degradation mechanisms of dioxins and DDT were different.

2005-P12

白色腐朽菌によるダイオキシン汚染土壌の処理

原田和寿[*1]、亀井一郎[*1]、近藤隆一郎[*2]
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Biodegradation of polychlorinated dioxin-polluted soil by white-rot fungi

Kazuhisa Harada[*1], Ichiro Kamei[*1], Ryuichiro Kondo[*2]
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Abstract: 1,3.6,8-tetrachlorodibenzo-*p*-dioxin (1,3,6,8-tetraCDD) is a main contaminant of contaminated paddy soil. Therefore, the removal of 1,3.6,8-tetraCDD is the key component of decontamination. Recently, we showed that 1,3,6,8-tetraCDD was transformed by *Phlebia brevispora*, and 2-methoxy-1,3,6,8-tetraCDD and 3.5-dichlorocatechol were detected as metabolites1). In this study, we attempted the degradation of 2.7-dichlorodibenzo-*p*-dioxin (2,7-diCDD) and 1,3,6,8-tetraCDD in soil. Forty six% of 1,3,6,8-tetraCDD in artificially contaminated soil were degraded by the treatment with *P. brevispora* for 14 days. And also, we identified the metabolites from 2,7-diCDD and 1.3,6,8-tetraCDD in artificially contaminated soil by treatment with *P. brevispora*.

2005-P13

アンモニウム残基を有するリグニン誘導体とクレーを原料とする複合体の調製

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[*1] 産業技術総合研究所、[*2] 福井工業大学工学部

Preparation of composites consisting of lignin derivative with ammonium residue and clay

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Abstract: Kraft lignin was allowed to react with glycidyltrimethylammonium chloride in polyethylene glycol 400 (molecular weight 400) in the presence of catalytic amount of dimethylbenzylamine at 100 ºC for 12 h. The obtained reaction product was mixed with montmorillonite at room temperature. The obtained composites were allowed to stand for 1 day at 60 ºC. The composites were studied by Fourier transfer infrared spectroscopy (FTIR). The thermal properties of the composites were also studied by differential scanning calorimetry (DSC) and thermogravimetry (TG).

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2006-101

高分子リグニン酸化能力を有するペルオキシダーゼアイソザイム CWPO−C の機能解析

佐々木慎弥、野中大輔、割石博之、堤祐司、近藤隆一郎
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The rote of the Tyr on the protein surface of cationic cell-wall-peroxidase

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Abstract: A unique peroxidase isoenzyme, cationic cell-wall-peroxidase (CWPO-C), from poplar callus oxidizes sinapyl alcohol, ferrocytochrome *c* and synthetic lignin polymers, unlike other plant peroxidases. Here, the catalytic mechanism of CWPO-C was investigated using chemical modification and homology modeling. Tyr modification of CWPO-C strongly suppressed its oxidation activities toward syringaldazine and 2,6-DMP by 90%, and also suppressed its guaiacol oxidation activity to a Iesser extent. Ferrocytochrome c was not oxidized by TNM-modified CWPO-C. These resu[ts strongly suggest that Tyr residues in CWPO-C mediate its oxidation of syringyl compounds and high-molecular-weight substrates. Homology modeling indicated that Tyr-177 and Tyr-74 were
located at the protein surface of CWPO-C and near the heme. These results suggest that Tyr residue on the protein surface is a key player in CWPO-C for its wide substrate oxidation spectrum.

2006-102

Characterization of *Carthamus tinctorius* cinnamyl alcohol dehydrogenases

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Abstract: Characterization of three genes encoding cinnamyl alcohol dehydrogenase in *Carthamus tinctorius* was carried out. Gas chromatography-mass spectrometry based enzyme analysis and substrate level enzyme kinetics show that two *Carthamus tinctorius* cinnamyl alcohol dehydrogenases (CtCADs), named CtCAD1 and CtCAD2, respectively, have a slightly different kinetic character. Lineweaver-Burk kinetic analysis shows that CtCADl and CtCAD2 have almost the same catalytic activity towards coniferaldehyde and sinapaldehyde. Inhibition assay of CtCAD1 shows that the reduction of coniferyaldehyde is inhibited by the presence of sinapaldehyde. In contrast, inhibition assay of CtCAD2 showed inhibition of both coniferaldehyde and sinapaldehyde reduction. The results show that CtCAD1 and CtCAD2 play an important role in the formation of both syringyl and guaiacyl monolignols. The characterization of another CtCAD (CtCAD3) is currently underway.

2006-103

イネをモデルとした植物細胞壁形成過程に関する研究 —Glosylphosphatidylinositol はイネの細胞壁高次構造形成にどのように関わるのか？−2

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Study of plant cell wall formation in *Oryza sativa* L. — How does glosylphosphatidylinositol-anchored protein relate to cell wall conformation in rice plant (*Oryza satiba* L.)?-2

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Abstract: There are many studies about cell wall formation using mutant. However, most of them are about biosynthesis of main cell wall component such as cellulose, hemicellulose, and lignin. Few information obtained about detailed mechanism and process of wall conformation. In this study, we used brittle culm mutant called 'cwa1', recessive mutant rice plant (*Oryaza sativa* L.). Cwal has defective in plant mechanical strength.

But there is a little distinction of amount of cell wall components. And it's revealed that cwa1 has defective cell wall thickness, and distribution of wall components by histological analysis. So cwa1 is predicted that it has defective in cell wall conformation after cell wall components are biosynthesized. By analyzing cwa1 and its' defective gene, *BC1*, we can discuss about mechanism and process of cell wall conformation in monnocot..

2006-104

ポプラにおける細胞膜を介したモノリグノール輸送メカニズム

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Mechanism of monolignol transportation through plasma membrane in poplar

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Abstract: The lignin biosynthesis consists of three parts, that is, biosynthesis, transportation, and polymerization of monolignols. Recent investigation shows that the enzymes, involved in conversion of the last step of monolignol biosynthesis, localize in cyto-sol. Therefore, monolignols probably exist in cytosol. They may be transported from cyto-sol to cell wall via plasma membrane and then polymerized within the cell wall. In this study, we analyzed the mechanism of monolignol transportation in lignifying tissues. The characterization of monolignol transport using microsomal fractions containing membrane vesicles showed that uptake of coniferin was stimulated by Mg/ATP, while that of coniferyl alcohol, sinapyl alcohol and syringin were little regardless of presence of ATP. Coniferin uptake was strongly inhibited with $NH4^+$, while vanadate, which was commonly used to inhibit ATP-binding cassette (ABC) transporters, had no effect. This suggests that coniferin uptake
into membrane vesicles depends on the electrochemical gradient of H^+ across them.

2006-105

リグナン生合成経路におけるメチレンジオキシブリッジ形成と配糖化反応

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Methylenedioxy bridge formation and glucosylation in lignan biosynthesis

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Abstract: (+)-Sesamin, a furofuran class lignan, is widespread in vascular plants and represented by *Sesamum* spp. (+)-Sesamin has been of rapidly growing interest because of its beneficial biological effects in mammals, but its biosynthesis and physiological roles in plants remains to be clarified. It is speculated to be synthesized from (+)-pinoresinol via (+)-piperitol by formation of two methylnedioxy bridges mediated by two distinct *Sesamum indicum* cytochrome P450 proteins. Here we report a novel *S. indicum* P450, CYP81Q1 that alone catalyzes (+)-sesamin biosynthesis from (+)-pinoresinol via (+)-piperitol by forming two methylenedioxy bridges. The CYP81Q1 gene expression profile was temporally consistent with the accumulation pattern of (+)-sesamin during seed development. The CYP81Q1-GFP chimera protein was co-localized with an endoplasmic
reticulum (ER) targethg chimera protein, indicative that (+)-sesamin biosynthesis occurs on the ER cytoplasmic surface. Moreover, we isolated two CYP81Q1 homologs from other *Sesamum* spp. *S. radiatum* CYP81Q2 showed the dual (+)-piperitol/(+)-sesamin synthetic activity. CYP81Q2 as well as CYP81Q1, therefore corresponds to an (+)-piperitol/(+)-sesamin synthase (PSS) in lignan biosynthesis. In contrast, *S. alatum* CYP81Q3 showed no activity, in accord with (+)-sesamin being deficient in *S. alatum*. Our findings not only provide new insight into lignan biosynthesis but also
unravel a novel mode of cytochrome P450 action.

2006-106

分化中木部における細胞壁成分の ToF−SIMS イメージング

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ToF-SIMS imaging of constituents in plant cell walls of differentiating xylem

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Abstract: Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used to visualize the distribution of lignin and polysaccharides in the differentiating xylem of *Pinus thunbergii*. A recent study using ToF-SIMS showed that lignin polymers can be characterized by specific secondary cations with a guaiacyl ring at m/z 137 and 151. In this study, the specific monomeric ions of cellulose and xylan were also identified. ToF-SIMS imaging analysis showed that the image of deposition of cellulose and xylan disappeared after that the image of deposition of lignin started in the differentiating xylem.

2006-107

リグニン β−O−4 構造の細胞壁における絶対量と細胞壁「木質化」との関係

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Absolute Amounts of β-O-4 structures in wood and non-wood cell walls

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Abstract: All higher vascular plants, whether they are wood species or not, contain lignin in the cell walls, but wood cell walls are much harder and stronger than non-wood cell walls such as leaves and grasses. The important key factor for cell walls to be hard and have enough strength is still unknown. The purpose of this investigation is to understand the difference between wood cell wall and non-wood cell wall such as of leaves and grasses from viewpoints of lignin structure and its content. As a measure to distinguish wood cell walls and non-wood cell walls, we examined the absolute amount of arylglycerol-β-aryl ether (β-O-4) structure in cell wall, not in lignin, by ozonation method. It seems that a critical level is present for the amount of β-O-4 structures in wood cell wall and this level gradually increased depending on the syringyl ratio. Interestingly, this amount found for all the leaves and most of the grass stems was lower than this critical level. We will hypothetically propose the importance of the absolute amount of β-O-4 structure in cell wall, not in lignin, to distinguish wood cell and non-wood cell.

2006-108

モノリグノール配糖体の HRP 触媒脱水素重合 Part 2.

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HRP catalyzed dehyrogenative polymerizations of monolignol glucosides. Part 2.

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Abstract: Dehydrogenative polymerizations of monolignol β–D-glucosides (isoconiferin, **1a**; isosyringin, 1b; triandrin, **1c**) using horseradish peroxidase (HRP)/ H_20_2 as catalyst were carried out, resulting in the formations of water-soluble lignin-like polymers (DHPs): poly (1a)-(**1c**), The degrees of polymerization (DPs) of poly (**1a**) and poly (**1c**) were much higher than those of conventional DHPs, whereas DP of poly (**1c**) was low. Cyclic voltammetry analyses showed that the monomer **1b** had a lower oxidation potential than monomer **1a** and **1b**. HRP-catalyzed initial reaction rates of monomer **1b**, however, was extremely low and in the same range as that of sinapyl alcohol, while the oxidation rates of monomer **1a** and **1c** were significantly higher than those of corresponding monolignols. These results indicated that HRP had low specificity to monomer **1b** as well as to sinapyl alcohol and did not catalyze the formation of highly polymerized poly (**1b**) even in a homogeneous reaction system. Structural analyses confirmed that poly (**1a**)-(**1c**) were lignin-like polymers containing D-glucose units attached to the lignin sidechains.

2006-109

高速フローESR 法を用いたリグニンモデル化合物に対するラジカル種の反応性に関する研究

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Studies on reactivity of radical species with lignin model compounds using a rapid flow-ESR method

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Abstract: It has been discussed that non-phenolic lignin model compounds (LMCs) are degraded by radical reactions. In the reactions with free radicals, it is suggested that extraction of electron or hydrogen atom from the LMCs are induced by the radicals. However, there has been no direct spectroscopic evidence demonstrating the production of initial radical intermediates from the LMCs by the free-radical-mediated degradation. Furthermore, it was not shown which radical species can degrade the LMCs. In the present study, we tried to detect the radicals derived from the LMCs produced by the reactions with alkoxyl, peroxyl, hydroxyl and hydroperoxyl radicals using a rapid flow-ESR method. The results suggested that peroxyl and hydroperoxyl radicals have no reactivity with the LMCs. On the other hand, hydroxyl radicals extract a hydrogen atom from the a position of veratryl alcohol (VA), a simplest monomeric LMC used. ESR spectrum of this radical was quite different from the radical produced by one electron extraction with Ce^{4+}.

2006-110

耐塩性白色腐朽菌 *Phlebia* sp. MG60 の産生するマンガンペルオキシダーゼの発現解析

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Expressional analysis of manganese peroxidases from saline-tolerant white rot fungus, *Phlebia* sp. MG60

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Abstract: Expression pattern of manganese peroxidases (MnPs) which were produced by saline- tolerant white rot fungus, *Phlebia* sp. MG-60, was analyzed. When MG-60 was cultured in the Kirk medium containing 3% sea salts (salt medium), higher activity of MnPs was produced than that in the normal Kirk medium (0% sea salts). SDS-PAGE analysis demonstrated that two MnP isoenzymes were *de novo* synthesized during the culture in the salts medium. Three MnP encoding genes (*MG-mnp1, MG-mnp2, and MG-mnp3*) were isolated and these transcriptions in the Kirk medium with and without 2% NaCl were determined by real-time PCR technique. *MG-mnp2*, and *MG-mnp3* were highly expressed in the medium with NaCl.

2006-111

アカシアクラフトパルプのバイオブリーチングに向けた白色腐朽菌のスクリーニング

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Screening of white rot fungi and their potential application in biobleaching of acacia kraft pulp

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Abstract: To study the biobleaching to Acacia kraft pulp, over 600 strains of white rot fungi were collected from various natural sources such as fruiting bodies, rotten woods and trap piles at various locations in Indonesia such as West Java, Central Kalimantan, South Kalimantan, Jambi and North Sumatra. We succeeded to screen five strains of white rot fungi for application in Acacia kraft pulp bleaching.

2006-112

担子菌におけるヘム生合成の特異的制御機構

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Molecular mechanisms involved in the regulation of heme biosynthesis in *Phanerochaete chrysosporium*

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Abstract: Addition of exogenous aromatic compounds to *Phanerochaete chrysosporium* resulted in an immediate metabolic shift from a short-cut TCA/glyoxylate bicycle system into a general TCA cycle, which in turn resulted in the activation of the heme biosynthetic pathway branched at succiny1-CoA. On the other hand, a free heme is highly toxic to the cell. To reveal regulatory mechanisms involved in fungal heme biosynthesis, a comprehensive analysis for surveying heme- binding proteins produced by *P. chrysosporium* was performed. Biotinylated heme- streptavidin beads system was utilized for separating intracellular heme-binding proteins. From an SDS-PAGE separation and MALDI/TOF-MS analysis on peptide mass fingerprinting of these proteins, mitochondrial citrate synthase (PcCS) and glycelaldehyde 3-phosphate dehydrogenase (PcGAPDH) were identified as putative heme-binding proteins. Recombinant PcCS and PcGAPDH were expressed as active forms in *E. coli* for further kinetic and spectroscopic characterization. Either PcCS or PcGAPDH was inhibited with a physiological concentration of hemin. Inhibitory mechanism was further characterized for PcCS using a homology modeling technique. These observations were the first evidence for a direct interaction of a heme molecule to metabolic enzymes to control a metabolic flux in the fungus.

2006-113

The oxidation of polyphenols by extracelullar peroxidase from suspension cultured cells of liverwort *Heteroscyphus planus*

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Abstract: Suspension cultured cells of liverwort, *Heteroscyphus planus* excreted peroxidase in the culture medium. The peroxidase activities were inducted by co-incubation of phenols such as *p*-cresol, 2,6-dimethoxyphenol, bisphenol-A (BPA) and lignin model compound (LMC, guaiacylglycerol-β–guaiacyl ether). We observed the oxidation of BPA and LMC in the cultured cells of the liverwort. BPA was mainly polymerized to higher molecular compounds, while was partly biodegraded to small molecular compounds. The biodegraded compounds were identified as 4-isopropenyl and *p*-hydroxyacetophenone. The process to form these compounds was examined using deuterated-BPA. LMC was degraded to guaiacol, vanillin, coniferyl alcohol and ferulic acid, while a dimmer of LMC, 1,1'-(4,4'-dihydroxy-3,3'-dimethoxy-5,5'-biphenylene)-bis [8-(2''-methoxy- phenoxy)-7,9-propanediol] was also detected.

2006-特別講演 I

Invited Lecture, I

Biotechnology based wood quality research program for forest biorefinery

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Introduction: The Southern U.S. is the major supplier of industrial wood and wood products to the world. North Carolina State University, in collaboration with industry and governmental agencies, has been undertaking an intensive breeding program for loblolly pine during the past fifty year, resulting in great increase in growth, straightness, wood density and disease resistance. In anticipation of ever increased demand for wood in the future, increasingly intensive plantation forestry is being used for wood supply. Great increases in the productivity of pine plantations in the southern US have been achieved due to genetic and silvicultural improvements in recent years. However, increased growth rates have resulted in trees with more juvenile wood, many properties of which are quite different from those of mature wood. We thus focus our efforts for the production of rapid growing short rotation juvenile loblolly pine with improved wood properties. To achieve this goal, we have been integrating research on wood properties, tree breeding, propagation and genomics during the past 8 years. Two approaches have been taken to achieve this goal: selection of the desired traits from the genetically controlled natural variations in target properties and improvement through genetic profiling of the desired properties. On the other hand, recent sharp increase in the price of oil has greatly stimulated great interest in biofuel production. Several barriers still exist in converting lignocellulosic feed stock to biofuel.

During the past two years, we have been undertaking study to overcome some of the barriers by lowering lignin content and increase syringylpropane to guaiacylpropane ratio (S/G) using transgenic approach. In this presentation, we attempt to briefly describe our efforts and summarize the results in these two areas of research.

2006-201

リグニンの立体化学と微生物代謝機能に関する研究（I） −guaiacylglycerol-β-gaiacylether（GGE）の立体化学−

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Studies on stereochemistry of lignin and microbial metabolic functions - Stereochemistry of lignin and microbial metabolic functions -Stereochemistry of guaiacylglycerol-β–guaiacyl ether (GGE)-

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Abstract: Four stereoisomers of guaiacylglycerol-β-guaiacyl ether (GGE:1), which is important substrate for understanding the relationship between microbial metabolic functions and stereochemistry of lignin, were synthesized with enantiopure form. And two stereoisomers of α-(2-methoxyphenyl)- β-hydroxypropiophenone (MPHPV:2), which is important intermediate located in metabolic pathway of GGE microbial degradation, were also synthesized.

2006-202

リグニンの立体化学と微生物代謝機能に関する研究（II） ーバクテリアの立体選択的グルタチオン−*S*−トランスフエラーゼによる β-アリールエーテル開裂機構−

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Studies on stereochemistry of lignin and microbial metabolic functions (II): Cleavage of the β–aryl ether linkage catalyzed by bacterial enantioselective glutathione S-transferases

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Abstract: Cleavage of the β-aryl ether linkage is the most important process in lignin degradation. In a previous study, we isolated the β-aryl ether degradation operon, *ligDFEG*, of *Sphingomonas paucimobilis* SYK-6. The *ligD* gene encodes Ca-dehydrogenase, which oxidizes guaiacylglycerol-β-guaiacyl ether (GGE) to a-(2-methoxyphenoxy)- β-hydroxypropiovanillone (MPHPV). The *ligE*, *ligF*, and *ligG* genes showed similarity with glutathione S-transferases but only the gene products of *ligE* and *ligF* exhibited the β-etherase activity. In this study, we determined the actual roles of three GST genes. MPHPV was transformed by LigE and LigF to guaiacol and α-glutathionyl-β-hydroxy- propiovanillone (GS-HPV), suggesting that LigE and LigF catalyze the nucleophilic attack of glutathione on the carbon atom at the β position of MPHPV. HPLC-circular dichroism analysis indicated that LigE and LigF each attacked a different enantiomer of the racemic MPHPV preparation. LigG catalyzed the elimination of glutathione from GS-HPV generated by the action of LigF. Disruption of ligE, *ligF*, and *ligG* in SYK-6 showed that *ligF* is essential to the degradation of one of the MPHPV enantiomers. The alternative activities which metabolize the substrates of LigE and LigG are present in this strain.

2006-203

超臨界・亜臨界水条件での嘲 Björkman リグニンおよび微生物変性リグニンの反応

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Reaction of Björkman lignin and biologically modified lignin under supercritical and sub-critical water condition

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Abstract: Behavior of dissolved organic matters (DOM) in water, which was isolated from peat swamp water and characterised as biologically modifled lignin, under condition at deep sea would be quite important for global carbon circulation. Reaction of DOM under supercritical water condition (650K, 22.4MPa) was investigated together with those of Björknan lignins isolated from *Abies firma* and *Fagus crenata*. Demethylation reaction was predominant, and major products were catechol derivatives.

2006-204

フェノール性 β–エーテル型２量体モデル化合物の熱分解開裂機構に及ぼす Cγ–水酸基の影響

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Influence of Cγ-hydroxyl group on the mechanism of pyrolytic β-ether cleavage of phenolic model dimers

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Abstract: We already reported that elimination of the Cγ-OH group substantially inhibited the pyrolytic cleavage of the β-ether bond of phenolic model dimers. The temperatures where model dimmers became reactive in 1 min pyrolysis were different between Cγ-OH type (250ºC) and Cγ-deoxy type (400ºC). These previous findings indicate that cleavage mechanisms are different between these model dimers. In this paper, these cleavage mechanisms are discussed. Reactivity of the Cγ-deoxy type was very dependent on the pyrolysis conditions. Cγ-deoxy type was stable even at 400ºC under the conditions which made the volatilization of low molecular weight (MW) products from the heated zone easy. On the other hand, the Cγ-deoxy type was completely decomposed at 400ºC and even reactive at 300ºC when model compound in a closed ampoule was heated in muffle furnace. These results indicate that radical chain reaction occurs in pyrolysis of the Cγ-deoxy type. To confirm this, influence of tetralin (a radical scavenger) was investigated for Cγ-deoxy and Cγ-OH types of model dimers. As a result, addition of tetralin substantially reduced the pyrolytic cleavage reactivity of the Cγ-deoxy type, whereas the reactivity of the Cγ-OH type was not influenced by tetralin. Furthermore, reactivities of variously *p*-substituted model dimers (Cγ-deoxy type) in sufficient amount of tetralin increased positively related to the order of ABDE of the substituent groups. These results suggest the radical chain mechanism starting from the direct homolytic Cβ-O bond cleavage for the Cγ-deoxy type, although the β-ether bond of the Cγ-OH type is cleaved through quinonemethide formation (an ionic reaction) at much lower temperature of 250ºC. The role of the Cγ-OH group is also proposed as stabilizing effect of the transition state in quinonemethide formation by hydrogen bonds between Cα- and Cγ-OH groups. Under pyrolysis conditions, such intramolecular stabilization may play an important role in promoting the ionic type of reaction.

2006-205

酸素漂白条件下における活性酸素種による糖の被攻撃部位の特定（1）～アノマー位についての検討～

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Specification of the site of carbohydrate attacked by active oxygen species under oxygen bleaching conditions (1) - Examination on the anomeric position -

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Abstract: It has still been the serious problem that oxygen delignification is accompanied by the depolymerization of carbohydrates. It is important to know the degradation mechanism of carbohydrates to protect them under oxygen bleaching conditions. In this study, the relative reactivity of active oxygen species (AOS) toward two carbohydrate model compounds, methyl α-D-glucopyranoside (MGPα) and methyl β-D-glucopyranoside (MGPβ), was examined under practical oxygen bleaching conditions, where AOS were in situ generated by subjecting a phenolic compound, 2,4,6-trimethylphenol, to the oxygen oxidation. It was also examined whether or not the anomeric position is attacked by AOS by using a model compound, methyl β-D-[1-d]-gluco- pyranoside (MGPβ[1-d]). As the degradation of MGPβwas greater than MGPαat pH 13.5, it is suggested that the stereo configurational difference in their anomeric positions has an influence on their reactions with AOS. And the result that the reactivity of AOS toward MGPβwas higher than that toward

MGPβ[1-d], suggests a possible occurrence of the attack on the anomeric position.

2006-206

生命科学と有機材料科学を基盤としたリグニンの新しい高度利用に関する研究（I）

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Studies on the novel advanced utilization system of lignin based on the life science and organic material chemistry (I)

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Abstract: *Sphingomonas paucimobilis* SYK-6, which can degrade various low molecular weight compounds derived from plant polyphenols such as lignin, lignan, and tannin, metabolizes these substances via 2-pyrone-4,6-dicarboxylic acid (PDC). We focused on this metabolic intermediate as a potential raw material for novel biopolymers. We cloned the *ligAB* and *ligC* genes of SYK-6, which respectively encode protocatechuate 4,5-dioxygenase and4-carboxy-2-hydroxymuconate-6-semi- aldehyde dehydrogenase, into a broad host-range plasmid vector, pKT230MC. The resulting plasmid, pDVABC, was introduced into the PpY1100 strain of *Pseudomonas putida*, and we found that PDC could be stably produced from protocatechuate and accumulated. In addition, we examined the efficiency of production of PDC from protocatechuate on a 5-L scale in a LB-medium containing 100 mM glucose, and determined that PDC was stably produced from protocatechuate to yield 10g/L or more.

2006-207

生命科学と有機材料科学を基盤としたリグニンの新しい高度利用に関する研究（II）

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Studies on the novel advanced utilization system of lignin based on the life science and organic material chemistry (II)

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Abstract: 2-Pyrane-4,6-dicarboxylic acid (PDC) is an intermediate metabolite of *Sphingomonas paucimobilis* SYK-6 which can degrade and assimilate low molecular lignin. PDC can be used as polymer materials. We decided to product PDC using genetic engineering. For practical use, we tried to product PDC from various kinds of low molecular lignin in large scale. We finally product PDC in 5L scale from vanillin, vanillate, syringate and *p*-hydroxybenzoate which were provided from chemical treatment of lignin. In addition, we tried to product PDC from terephthalate which can obtain easily and cheaply. And now, we can product PDC from 10g/l of terephthalate. It helps to develop PDC application.

2006-208

リグノスルホン酸系硬質ポリウレタンフォームの発泡速度制御と熱的・機械的性質

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Effect of reaction rate on thermal and mechanical properties of sodium lingnosulufonate-based polyurethane foams

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Abstract: Sodium ligninosulfonate (NaLS)-based polyurethane (PU) foams were prepared using three

kinds of ethylene glycols, such as diethylene glyco1, triethylene glycol or polyethylene glycol. Two kinds of NaLS, weak acid based NaLS(WA) and weak alkaline based NaLS (WB), were used in order to control the foaming reaction. Stirring time, cream time and rise time were used as an index of foaming reaction. Mixing time was defined as a time interval from adding MDI to detect evolved heat under stirring, cream time as a time interval from termination of stirring to starting of foaming, and rise time as a time interval from starting to completion of foaming. The above reaction times increased with increasing the amount of NaLS (WA) content in polyols. Apparent density, compression strength and compression modulus of PU foams linearly increased with reaction times. At the same time, the molecular mass of ethylene glycols markedly affects the molecular motion of PU foams. It was found that mechanical and thermal properties of PU foams are controllable through foaming reaction rate.

2006-209

リグニンスルホン酸塩を原料とするエステル型エポキシ樹脂の合成と熱的性質

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Synthesis and thermal properties of epoxy resins from ligninsulfonate

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Abstract: Sodium ligninsulfonate (LS) was dissolved in ethylene glyco1 (EG) and the obtained mixture was allowed to react with succinic anhydride to form a mixture of ester-carboxylic acid derivatives (LS-EG polyacid, LSEGPA). EG-polyacid (EGPA) was also prepared from EG. The mixture of LSEGPA and EGPA was reacted with ethylene glycol diglycidyl ether in the presence of catalytic amount of dimethylbenzylamine to form epoxy resins. The molar ratio of epoxy groups to carboxylic acid groups ([EPOXY]/[AA] ratios, mol/mol) was maintained at 1.1. The contents of LSEGPA in the mixture of LSEGPA and EGPA (LSEGPA content) were varied from 0 to 100 %. Thermal properties of epoxy resins were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG). Glass transition temperatures (*Tg's*) of epoxy resins increased with increasing LSEGPA contents suggesting that lignin acts as a hard segment in epoxy resin networks. Thermal decomposition temperatures (*Td's*) of epoxy resins were almost constant regardless of LSEGPA contents.

2006-210

リグノスルフォン酸をベースとしたポリカプロラクトン誘導体の物性と生分解性について

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Effect of biodegradation on thermal and spectroscopic properties of lignosulfonate-based polycaprolactone derivatives

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Abstract: Lignosulfonate-based poly caprolactone (L-PCL) specimens were subjected to biodegradation in the field. Spectroscopic and thermal properties of the recovered samples were analyzed with FTIR and DSC. The results suggested that ester moieties in L-PCL were more rapidly degraded than lignin moieties. The alternative experiment with MODA (Micobial Oxidative Degradation Analyzer) recently developed indicated that sucrose linked with PCL was decomposed to CO_2 much faster than L-PCL and cellulose.

2006-211

環状カーボネート／グリコール系加溶媒分解で得られるリグニンの化学構造と熱特性

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Chemical structure and thermal properties of the Llgnin fraction prepared by the solvolysis using cyclic carbonate/glycol systems

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Abstract: A new solvolysis system is being proposed for the bioconversion of lignocellulosics to valuable chemicals and materials in FFPRl. Using the solvolysis systems of cyclic carbonates/glycol, our system can convert lignocellulose into levulinates with high conversion rates, and moldable lignin fraction, During this process, glycol chains that have high thermal mobility are introduced into the lignin molecules by the reaction with both of cyclic carbonates and glycols. With extent of reaction period, average length of ethylene glycol chain is extended, and GPC average molecular weight is increased. The amount of introduced glycol chain can be estimated by quantitative ^{13}C-NMR with relaxation reagent, UV and thermogravimetric analysis.

2006-212

オルガノソルブリグニン（アセテート）／セルロース親和性ポリマー複合体の分子間相互作用の評価と木材・紙用速乾性接着剤としての応用

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Interaction in organosolv lignin and its acetate with synthetic polymers comprising vinyl pyrrolidone unit

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Abstract: Binary blends and pseudo complexes of organosolv lignin (OSL) and acetylated OSL with poly(N-vinyl pyrrolidone) (PVP) and poly(N-vinyl pyrrolidone-*co*-vinyl acetate) (PVPVAc) were prepared, respectively, by casting from mixed polymer solution in NN-dimethylformaide as good solvent and by spontaneous co-precipitation from solutions in tetrahydrofuran as comparatively poor solvent. Miscibility and intermolecular interaction of the blends were investigated by means of DSC and FT-IR. FT-IR spectra revealed the presence of hydrogen-bonding interactions between hydroxyl groups of OSL and carbonyl groups of N-vinyl pyrrolidone units. Thermal transition data obtained in the DSC analysis clarified that the blends of the two polymers exhibited decidedly a single and composition-dependant *Tg* between the *Tgs* of the individual components. This observation demonstrates that the blend system is miscible. The existences of both the hydroxyl group in OSL and VP unit in vinyl polymers were essential for the emergence of miscibility and the formation of pseudo-complexes.

2006-213

針葉樹パルプ製造とバイオエネルギー生産における国産カラマツ材の有効利用

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Effective utilization of Japanese *Larix leptolepis* wood for production of softwood pulp and bio-energy

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Abstract: Eighty seven percent of the afforestation area in Japan is coniferous forest. For the effective production of pulp and bio-energy, the kraft and soda pulp yieldsof Japanese major planted softwoods (*Larix leptolepis*, *Pinus densiflora*, *Cryptomeria japonica*) were investigated, and compared those of imported hardwoods (*Acacia, Eucalyptus*). The softwood pulp yields at a kraft pulp mill were estimated by a method based on the ratios of mannose to glucose from pulps. The organic elements components in the black liquors were estimated for their utilization as bio-energy.

2006-214

リグニンによる転写因子 NF−□B の活性化の抑制

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Lignin suppresses NF-□B activation in 293-T cells

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Abstract: Transcription factor NF-kB controls cell functions such as apoptosis, inflammation, the immune response, cell growth, differentiation, and chronic infection with human immunodeficiency virus type 1(HIV-1). Activation of NF-□B by external stimuli such as tumor necrosis factor α(TNFα) and its binding to long terminal repeat (LTR) of HIV-1 triggers the initiation of transcription of viral genes. In this study, we use several lignins to show that lignins inhibit expression of NF-□B and LTR(HIV-1) reporter genes. Low molecular weight lignins (800>) were more effective rather than high molecular weight lignins. Furthermore, we exhibit that a β-5 lignin model compound shows stronger inhibitory activity than β-*O*-4 lignin model compounds. These results suggest that low molecular weight lignins (dimmer or trimer?) suppress HIV-1 replication and NF-□B activation, and that lignin could be lead-compound for medical drugs.

2006-215

酢酸リグニンの工業利用に関する研究

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A study for industrial utilization of acetic acid lignin

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Abstract: Attempts were made to utilize palm oil residues with acetic acid pulping process under atmospheric pressure. Empty fruit bunch, herein after called EFB, of the oil palm was digested into pulp and acetic acid lignin, herein after called AL, through the process, since lignin reacted with and dissolved into acetic acid. Oil palm AL showed heat fusion characteristic and dissolved into organic solvents such as acetone and etc, as same manner as other ALs taken from ordinary woods. Board-shaped moldings were prepared from the pulp and the AL from EFB by proper pressurizing at around 170 degree C. Bending strength of the moldings was easily controlled by varying molding pressure and/or temperature or composition ratio between the pulp and the AL. Another attempt was made to prove termites repellent or termiticide of the AL. Cedar chips treated with diluted AL showed certain repellency and termiticide effect to suggest a new usage of the AL.

2006-特別講演 II

人工土壌マトリックスとしてのオガ屑 －リグニンの存在と意義－

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Invited Lecture, II

Sawdust as an artificial soil matrix for bioconversion of biomass wastes into multifunctional recyclables -Significance of the existence of lignin in sawdust-

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Abstract: Biomass wastes such as garbage (food oriented wastes), excreta, and livestock manure are effectively bio-converted into multifunctional recyclables in the GADE (garbage automatic decomposer-extinguisher), BT (bio-toilet, dry toilet or composting toilet), and LMF (livestock manure fixer) systems, respectively, using sawdust as an artificial soil matrix in the systems. Mushroom cultivation beds, anti-fire fiberboard, nutrition containing planting pots, pellets, packing materials, etc. are the multi-functional recyclables. High porosity of sawdust is the main function of sawdust, offering the high air retention and moderate water retention. High surface ratio of sawdust contributes the effective evaporation of water from the sawdust matrix. These characteristics keep the matrix aerobic conditions. Aerobic biodegradation of the organic matters in the wastes is essential for the odorless operation of the systems. High bacterial tolerance and high abrasion tolerance are caused from the existence of lignin in the matrix. Because of the existence of lignin, sawdust can be used for long period as the artificial soil matrix. Practical uses of sawdust will be introduced.

2006-P01

リグニンの α 位水酸基の生成と脱離に関する分子軌道解析

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Molecular orbital analysis on the formation and cleavage of α-hydroxyl group in lignin

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Abstract: To investigate the formation of α-hydroxyl group in lignin, the β-O-4 lignin model compounds were analyzed with an *ab initio* molecular orbital calculation using RB3LYP/6-31G* method. The optimum conformations were varied with the existence of methoxyl groups in B-ring. The electrostatic charges at α-carbon were negative value and similar in neutral quinonemethides. For cationic enol radicals of guaiacyl and syringyl models, the electrostatic charge at α-carbon transferred to positive value by protonation of ketone in quinonemethides. Also the HOMO-LUMO gaps were independent with the methoxyl groups but much decreased with protonation.

2006-P02

レジノール構造の生成に関する分子軌道解析

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Molecular orbital analysis on the formation of resinol structure

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Abstract: The reaction mecbanism in radical couplingr eaction of lignin was analyzed with a molecular orbital calculation. The cbarge density, the electrostatic potential and the spin density of monolignol radicals were determined with UB3LYP/6-31G* basis set. For the simulation in acid solution，the spin density at C_8 was increased by protonation of O_4. The transition states during radical coupling reaction were determined with semi-empirical molecular orbital calculation by using UPM3. The simulation on the reaction of cationic and neutral radicals of sinapyl alcohol demonstrated that β-O coupling dominantly produced compared witb β-β coupling. This computational result agrees with the experimental result that the production of β-O dimer increases in acid solution.

2006-P03

木材抽出成分の着色に関する計算化学シミュレーション

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Computer-chemical simulation on the coloration of woody extractives

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Abstract: To predict the color change of norlignans, UV/VIS spectra were simulated with the molecular orbital energies determined by an *ab initio* molecular orbital calculation (RB3LYP/6-31G*). Obtained spectra well expressed the coloration of sequirin-C involving the oxidation with enzyme, air or alkaline treatment; sequirin-C is the main component causing the blacking of sugi (*Cryptomeria japonica*) heartwood. We believe this simulation technique is useful for the prediction of UV/VIS spectrum of unknown or unpurified substances, and the chase of intermediates in various reaction pathways.

2006-P04

計算化学によるタンニン吸着機構の解析

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Computer-chemical analysis on the adsorption mechanism of tannin

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Abstract: The conformation, the dipole and the electrostatic potential of proanthocyanidins up to hexamer were computed with a semi-empirical molecular orbital calculation (RPM3). In the case of (4α-8)-catechins, the dipole increased with the degree of polymerization. This tendency was parallel to the experimental result in the precipitation of protein by fractionated bark tannin. For other proanthocyanidins, the dipoles of (4α-6)-catechins and (4β-8)-epicatechins were decreased at odd and even values, respectively, of the degree of polymerization.

2006-P05

リグニンの熱分解：β-O-4 構造単位由来の生成物

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Pyrolysis of lignin: Products stemming from β-O-4 subunits

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Abstract: Sources of pyrolysis products of lignin were investigated in conventional pyrolysis and in pyrolysis in the presence of tetramethylammonium hydroxide (TMAH) (TMAH thermochemolysis). To know the contribution of β-O-4 subunits to the pyrograms of lignins, a polymer (**I**, DPn 15.8), connected only by β-O-4 linkages, was subjected to both conventional pyrolysis (500ºC/4s) and TMAH thermochemolysis (315ºC/4s). Products were monitored by gas chromatography/mass spectrometry and compared with those of guaiacylglycerol-β-guaiacyl erther (**II**) and lignins (bulk dehydrogenation polymer of coniferyl alcohol and Japanese cedar wood lignin). **I** produced most of monomeric products observed in conventional pyrolysis and TMAH thermochemolysis. The results show that β-O-4 subunits make a large contribution to the lignin pyrograms obtained in conventional pyrolysis and TMAH thermochemolysis.

2006-P06

白色腐朽担子菌による PCB 代謝に関与するメチルトランスフエラーゼ

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Methyltransferase involved in PCB metabolism by white-rot fungi

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Abstract: Polychlorinated biphenyls (PCBs) are recalcitrant pollutants. Degradation experiment of model PCB compound, 4,4'-dichlorobipheny1 (4,4'-DCB) and its metabolites by white-rot fungus, *Phlebia brevispora* TMIC33929, which is capable of degrading a part of coplanar PCBs was carried out. The metabolic pathway of 4,4'-DCB was elucidated by the identification of metabolites upon addition of 4,4'-DCB and its metabolic intermediates. These results suggested the metabolic pathway was branched two pathways, a methylation pathway and a ring cleavage pathway, via initial metabolite, 3-hydroxy-4,4'-DCB. Of two pathways, the methylation pathway was predominantly compared to the ring cleavage pathway, and 3-methoxy-4,4'-DCB was decreased slowly. The conversion of 3-hydroxy-4,4'-DCB into 3-methoxy-4,4'-DCB was shown to occur by O methylation of 3-hydroxy-4,4'-DCB in a reaction catalyzed by S-adenosyl-L-methionine dependent O-methyltransferase.

2006-P07

白色腐朽菌からの微生物製剤作成の試み

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Attempts to make a microbial preparation from a white-rot fungus

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Abstract: In the present study, microbial preparation used several porous materials (zeolite, charcoal coated with ceramics, and wood) as basic materials were tried to prepare for bioremediation of dioxin-contaminated soil with white-rot fungi. The microbial preparations were made by adsorption of fungal biomass on the surface of porous materials. Furthermore, the microbial preparations were entrapped with calcium alginate gel. And the preparations were estimated by the decolonization ability on the agar plate impregnated with the dye as well as degradation rate of 2,4,8-Trichlorodibenzofuran (2,4,8-TCDF) in the soil. The degradation rate of 2,4,8-TCDF in the soil was only 10% for 30 days when the treatment with non-entrapped microbial preparation (zeolite) was conducted for 30 days. In contrast, 20% of 2,4,8-TCDF was degraded when the treatment with entrapped microbial preparations (zeolite and charcoal) was conducted for 30 days. These results suggest that bioremediation of dioxin-contaminated soil by microbial preparations made from white-rot fungi is possible.

2006-P08

ダイオキシン分解菌からの酵素を用いた酵素製剤作成の試み

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Attempts to make an enzyme preparation by crude enzyme from fungus capable of dioxins

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Abstract: Environmental pollution caused by endocrine disrupting chemicals (envirornental hormones) such as DDT [1,1,1-trichloro-2,2-bis (p-chlorophenyl) ethane] has become a major social problem. Therefore, several methods of dealing with environmental pollution have been proposed. Bioremediation with microorganisms or enzymes from the microorganisms is considered a most effective method of dealing with widespread pollution involving a low concentration of pollutant. In the present report, biodegradation of environmental hormones [DDT, 2,4,8-TCDF (2,4,8-trichloro- dibenzofuran) and TCB (3,3',4,4'-tetrachlorobiphenyl)] in water with a double capsule (an enzyme preparation) prepared from crude enzyme from fungi capable of dioxins, HBT(1-hydroxybenzo- triazole) and so on was conducted. The result showed that DDT, 2,4,8-TCDF and TCB could be degraded for 72 hours by the treatment. The rates of degradation were 50, 15 and 30%, respectively. In addition, environmental hormones (DDT, TCB) in soil were also degraded by the treatment.

2006-P09

ゴマの機能性リグナンの生合成、特にセサミノール配糖体等について

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Biosynthesis of functional lignans, particularly sesaminol glycosides, in *Sesamum indicum* seeds

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Abstract: Sesame seeds contain phenolic and antioxidant lignans such as sesaminol and pinoresinol, as well as sesamin and sesamolin. However, biosynthesis of the sesame lignans, particularly sesaminol and sesaminol glycosides was not clarified. In this study, feeding experiments of L-[U-^{14}C]phenylalanine (Phe) were carried out. A solution of L-[U-^{14}C]Phe (10 mM, 20 ml) was injected into unripe capsules of 11 week-old intact plants (*Sesame indicum* var. Mie-dai No.1 and *S. indicum* var. Chinese 36), and the plants were cultivated for a week at 26ºC. The radioactivity was incorporated into free sesaminol and sesaminol triglucoside and sesaminol diglucoside. The percent incorporation into sesaminol and sesaminol glycosides in seeds was eight times larger than that in the pods. In addition, the radioactivity was incorporated into 7-carbonyl type lignan glycoside in seeds

2006-P10

新規白色腐朽菌 *Phellinus* sp. SKM2102 株の脂肪酸不飽和化酵素遺伝子の単離・解析

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Characterization of fatty acid desaturase genes from a white-rot fungus, *Phellinus* sp. SKM2102

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Abstract: A new white-rot fungus, *Phellinus* sp. SKM2102, exhibits high pretreatment effects for enzymatic saccharification of wood similar to those of a selective lignin-degrading fungus, *Ceriporiopsis subvermispora*. However, profiles of their metabolites, such as fatty acids, are different, reflecting the differences of the gene expression involved in the fatty acid metabolism of these strains. We focus on the fatty acid metabolism, especially the biosynthesis of unsaturated fatty acids because unsaturated fatty acids are the precursors of lipid peroxidation in the selective lignin degradation by *C. subvermispora*. In order to investigate

the unsaturation of fatty acids, we have already cloned fatty acid desaturase genes from *C. subvermispora*. In this report, we cloned fatty acid desaturase genes from SKM2102 by PCR-based method.

2006-P11
フエルラ酸ステアリルの酵素触媒二次元重合
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Enzyme-catalyzed two-dimensional polymerization of stearylferulate
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Abstract: Two-dimensional polymerizadon is a novel approach which can bring improved control of monomer reactivity and orientation in the resulting polymer compared to the polymer by conventional method. A good p-A isotherm of Stearylferulate (FA18) was obtained on phosphate buffer (pH=6.5) as well as on ultrapure water, so FA18 was spread at an air-water interface on buffer solution, and polymerized with horseradish peroxidase (HRP) and H_2O_2 in dark. From the results of UV spectroscopic analysis, it was suggested that the two-dimensional polymerization afforded the polymer with different bond pattern from that of the conventional polymer.

2006-P12
リグニンモデル化合物の電気化学的酸化
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Electrooxidation of lignin model compounds
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Abstract: The anodic oxidation of a lignin model compound, 1-(4'-ethoxy-3'-methoxyphenyl) ethanol (1G) was investigated to introduce carbnyl group at a-position. Cyclic voltammetric measurements of 1G and other 1-phneyl ethanol derivatives, 1-(4'-ethoxy-3',5'-dimethoxyphenyl) ethanol (1S) and 1-(4'-ehoKyPhen9) ethanol (1 P), were performed to determine their redox potentials and compare electronic properties of nonphenolic G S, P substructures in lignins. The compound 1G was oxidized by bulk electrolysis in acetonitrile. In electrolysis without base, various side reactions occurred, and a-carbonyl product was obtained in low yield. Whereas, electrolysis with base or H_2O gave α-carbonyl derivative (2G) in high yield. The proposed electrooxidation mechanism of 1G is likely guideline for α-carbonyl introduction to neutral lignin structures.

2006-P13
植物細胞壁木化過程のシュミレーション、—ポリエチレングリコールを用いたシリンギルグリセロールーβーシナピルアルコールエーテルの合成—
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Simulation of plant cell wall lignification process - Dehydrogenative syringylglycerol-β-sinapyl alcohol ether in the presence of polyethylene glycol-
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Abstract: DHPs (dehydrogenative polymer of monolignols, artifical lignins) have been used as model compounds to clarify the chemical structure and the formation mechanism of lignins in plant cell walls. DHP of the sinapyl alcohol is remarkably different from lignin in the hardwood cell wall. For example, syringaresinol is formed mainly from the sinapyl alcohol with a small amount of β-O-4 type on using the mixed method polymerization. Also, in relating to the drop-wised method polymerization, lower molecular weight S-DHP including mainly β-βtype linkage are formed. It is therefore important to examine the polymerization condition of DHP for clarifying the biosynthesis mechanism of lignin in cell wall. We have succeeded to synthesize lignin containing a large amount of β-O-4 unit under the hydrophobic condition using the polysaccharide gel. In the paper, enzymatic dehydrogenative polymerization of sinapyl alcohol is tried under the hydrophobic condition using polyethylene glycol (PEG).

2006-P14

広葉樹硫酸リグニンのフェノール化に関する研究

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Study of phenolization of hardwood sulfuric acid lignin

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Abstract: To study the behavior of hardwood sulfuric acid lignin (SAL) during phenolization, we compared the product yield, average molecular weight, methoxy content, and reactions of simple model compounds with those of softwood SAL, focusing on the difference between syringyl and guaiacyl units. The beech SAL reacted with phenol more readily than red pine SAL and yielded a greater soluble fraction of phenolized SAL. To investigate the difference in the phenolization activity of the syringyl and guaiacyl units in beech lignin, we prepared syringyl-nucleus-rich sulfuric acid lignin (S-rich-SAL) and guaiacyl-nucleus-rich sulfuric acid lignin (G-rich-SAL) from beech, which were subjected to phenolization. The results suggest that the syringyl unit in SAL had greater phenolization activity and its phenolized products were more soluble in acidic aqueous medium and introduced less phenol than the guaiacyl unit to solubilize. The study using model compounds also showed that the syringyl unit had higher phenolization reactivity than the guaiacyl unit.

2006-P15

リグノクレゾールを利用した環境適合型接着剤の開発

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Development of environmental-friendly lignocresol-based adhesive

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Abstract: Biodegradable lignin-derivatives are gathering attention as a possible source for polymer materials. Lignocresol (LC) is produced through reactive extraction with *p*-cresol from lignin- containing wood, and is considered to be biomass-derived polyol since it has a number of phenolic and alcoholic hydroxyl groups. In this study, a polyurethane based adhesive was prepared from a ternary mixture of LC / polyethylene glycol (PEG) / Lysine triisocyanate (LTI) (2-Isocyanatethyl- 2,6-diisocyanatecaproate), and was applied for the bonding of wood. Satisfactory tensile share strength of over 10 MPa was obtained with the adhesive, indicating a promising use of LC as an ingredient of environmentally-friendly adhesives.

2006-P16

白色腐朽菌 *Phanerochaete sordida* YK-624 株の産生する菌体外ペプチド様物質の機能特性

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Functional characterization of peptide-like compound produced by white-rot fungus *Phanerochaete sordida* YK-624

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Abstract: White-rot fungus *Phanerochaete sordida* YK-624 produced a compound (YK-S) which inhibited the veratryl alcohol (VA) oxidation by novel lignin peroxidase (YK-LiP1) from this fungus. YK-S, which was produced under shaking culture, was purified to homogeneity by anion-exchange chromatography and gel permeation chromatography. By MALDI TOF-MS analysis, the molecular mass of YK-S was 1.822 Da, and YK-S contained 560 Da of peptide. Inhibitory effect of YK-S on VA oxidation by YK-LiP1 was investigated by Lineweaver-Burke plot in order to analyze the reaction mechanism of YK-S with YK-LiP1. YK-S inhibited VA oxidation by YK-LiP1 in a noncompetitive manner, and *Ki* Value of YK-S for YK-LiP1 was 103 mM. Moreover, the inactivation of YK-LiP1 by hydrogen peroxide was repressed under the presence of YK-S. These results strongly suggest that the role of YK-S is same as that of VA which functions as the substrate of Lip from *P. chrysosporium*.

2006-P17

バクテリアによるリグニン由来化合物代謝に関与する新規脱メチルシステム

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A novel tetrahydrofolate-dependent *O*-demethylation system in lignin metabolism by bacteria

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Abstract: The catabolism of vanillate and syringate by bacteria is an important process of the microbial lignin degradation. In *Sphingomonas paucimobilis* SYK-6, vanillate and syringate are converted into protocatechuate (PCA) and 3-*O*-methylgallate (3MGA), respectively, by *O*-demethylases. In this study, we isolated the *ligM* gene that conferred on *Escherichia coli* the activity required for the conversion of vanillate and 3MGA to PCA and gallate, respectively, with similar specific activities. The LigM catalyzes the transfer of the methyl moiety of vanillate to tetrahydrofolate (H_4folate), thereby forming PCA and 5-methyl-H_4folate. We demonstrated that PCA is not a growth substrate for SYK-6 cells, but we also showed that this strain is able to grow well on PCA in the presence of methionine. This finding suggested that the 5-methyl-H_4folate generated by the *O* demethylation of vanillate is essential for methionine biosynthesis. Downstream of *ligM*, two ORFs, which showed similarity with 5,10-methylene-H_4folate reductase gene (*metF*) and 10-formyl-H_4folate synthetase gene (*ligH*), were identified, and these genes were found to constitute an operon. These results indicated that the *O* demethylation of vanillate and the C_1 metabolism are simultaneously regulated in SYK-6. In conclusion, the *O* demethylation of vanillate catalyzed by LigM is important for SYK-6 cells, not only as a degradation step for vanillate, but also to supply the 5-methyl-H_4folate required for methionine biosynthesis.

2006-P18

バクテリアによるシリンガ酸代謝に関与するジオキシゲナーゼシステム

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The ring cleavage dioxygenase system involved in the syringate catabolic pathways in *Sphingomonas paucimobilis* SYK-6

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Abstract: *Sphingomonas paucimobilis* SYK-6 converts vanillate and syringate, which are intermediate metabolites of lignin, to protochatechuate (PCA) and 3-*O*-methylgallate (3MGA), respectively. Previous studies have indicated that PCA is further degraded by the reaction catalyzed by PCA 4,5-dioxygenase (LigAB) in PCA 4,5-cleavage pathway. In order to determine die ring cleavage pathways for syringate metabolism, we isolated and characterized the ring cleavage dioxygenase genes, *desZ* and *desB*, which confer the 3MGA and gallate degradation activities on *Escherichia coli*, respectively. Based on the analysis of enzymatic properties of these gene products and various SYK-6 mutants lacking die genes involved in the syringate degradation, we concluded that (i) all three-ring cleavage dioxygenases are involved in syringate catabolism, (ii) DesB and LigAB are involved in the degradation of gallate, and (iii) the pathway involving DesB plays an especially important role in the growth of SYK-6 on syringate.

2006-P19

樹木の細胞分裂制御に関する研究

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Research on cell division control of woody plant

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Abstract: As the largest storage organ in woody plants, it is of economic significance because most forest products are derived from the stem and help alleviate global warming by sequestering and storing carbons in long-term storage. Thickening of stem occurs as a result of growth and differentiation of secondary tissues produced by the vascular cambium. Therefore, control of cell division in vascular cambium leads to the improvement of woody resource production. In this study, we generated transgenic tobacco and poplar overexpressing CycD, E2F and DP-core cell cycle related genes and examined their influences for cell division, cell expansion, cell wall biosynthesis and lignification in secondary xylem. Moreover, as another approach of the cell division control, we try to solve the mechanism of an increase of the number of cells by suppression of genes. Here, we screened and analyzed a rice mutant that has many cells though growth normally.

2006-P20

シキミ酸経路を経由したグルコースからの2H-pyran-2-one--4,6-dicarboxylicacid（PDC）生産系の開発

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Biological conversion of glucose to 2H-pyran-2-one-4,6-dicarboxylic acid (PDC) by the bypassed shikimate pathways

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Abstract: PDC, 2H-pyran-2-one-4,6-diarboxylic acid, is one of metabolic intermediates in *Sphingomonas paucimobilis* SYK-6 that is a degrader of lignin-derived compounds. This compound has been also characterized as a raw material for synthetic polymers such as polyester and polyamide. In the previous study, we have already constructed the system on which PDC was efficiently converted from the aromatic compounds such as vanillic acid and vanillin in the recombinant microorganisms. In order to develop alternative system for PDC production, we try to produce the compound from glucose, which is one of low-cost sugars expected to be converted from abundant cellulose wastes and biomass crops. In the present study, we constructed two types of recombinant bacteria with the bypasses in their own shikimate pathways. By HPLC analysis, a trace amount of PDC that derived from glucose could be detected in the culture medium of the recombinant bacterium with *ubiC*, *pobA* and *LigABC*. Our result suggests that the bypassed shikimate pathway provide an alternative option for PDC production.

2006-P21

カワラタケ由来のラッカーゼ遺伝子を導入した組換え植物に見られる雄性不稔の解析

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Analysis of male sterility in the transgenic plants with the chimeric gene construct derived from the Trametes versicolor laccase gene

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Abstract: Laccase that require O_2 as secondary substrate can oxidize phenolic compounds. In the previous work, we have isolated a laccase cDNA, *CVL3*, from *Trametes versicolor* cDNA pool and generated transgenic tobacco plants in which a chimeric laccase gene was expressed under the control of cauliflower 35S promoter elements. Some of the transgenic plants overexpressing the gene could secret recombinant laccase protein from their roots. The secretory laccase activity in the plants was responsible for the transformation of phenolic compounds such as pentachlorophenol. Flowers of four transgenic lines, FL4, FL9, FL20 and FL22 with highly laccase activity exhibited mate sterile due to inhibition of anther maturation and dehiscence. Levels of laccase

activity in the anthers of these four transgenic plants have reached by over 6-fold increase as compared to that in wild-type plant. These results indicate that the laccase protein may play some physiological roles in anther development.

2006-P22

オゾン酸化を用いたリグニン系土壌改良剤の開発 II −オゾン酸化リグニンの酸化の程度と Al 毒性除去能との関係についての研究

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Development of lignin soil conditioning agent by ozone treatment II. -Studies on relationship between degree of oxidation and reduction of aluminum toxicity for ozone treated lignin

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Abstract: Relationship between degree of oxidation for oxidized lignin and its ability for the reduction of aluminum toxicity was examined in this study. The oxidized lignin samples were prepared by ozone or alkaline oxygen treatments. Degrees of oxidation for these samples were evaluated by permanganate consumption and methoxyl content after saponification. The lignin treated with ozone for 4h lost about 85% of methoxyl group, but the lignins treated by alkaline oxygen lost only about 4-14% of it. Both of them were, however, effective for reduction of aluminum toxicity. These facts were also confirmed by IR analysis. These results suggest that other factors, such as water-solubility or difference of reaction mechanism between ozone and alkaline oxygen, are more important than degree of oxidation for reduction of aluminum toxicity.

2006-P23

酸性下におけるリグニン β-O-4 結合開裂勝構の再評価（3） ー C_6-C_3 リグニンモデル合物を用いた解析ー

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Reevaluation of the mechanism for ale cleavage of lignin β-O-4 bond under acidic conditions (3) -Experiments using a C_6-C_3 model compound -

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Abstract: Acidolysis of lignin is a method used for structural analysis and isolation of liignin. The main reaction during acidolysis is the clavage of β-O-4 bond. According to the mechanism proposed by Lundquist et al., die rate-determining step of the reaction is the Abstraction of the β-proton from a benzyl cation substructure, resulting in the formation of an enol ether type substructure. Although other reports show die dependence of the cleavage rate on the kind of acid used, it is impossible to explain die dependence based on the mechanism proposed. Therefore, it is necessary to reinvestigate the reaction mechanism of acidolysis and analyze its kinetic. A dimeric non-phenolic lignin model compound, veratrylglycerol-β-guaiacyl ether (VG), was treated with HBr in 82% aqueous dioxane. It was found that the elimination of γ-position as formaldehyde does not occur in the system. This result is contrast with the known fact that die elimination of formaldehyde is occurred when HCl is used as a catalyst. It is suggested that HBr is more suitable than HCl as a catalyst of acidolysis.

2006-P24

熱帯産樹アテ材のリグニン化学構造

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Chemical tructure of lignin in reaction wood of tropical species

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Abstract: Reaction woods were obtained from leaning wood stems or branches of several tropical wood species and the relationships between the type of reaction wood and lignin characteristics was surveyed. As lignin characteristics, stereo structure of β-O-4 linkage (*erythro* ratio), aromatic ring type (syringyl ratio),

Klason lignin yield and acid soluble lignin content were determined. Tentatively, the relationships could be classified into 4 types. In all types, *erythro* ratio changed with clear tendency from the reaction wood part to opposite wood part, but the direction of the change was dependent on the type. In G-S lignin (guaiacyl-syringyl lignin) *erythro* ratio was highly correlated with syringyl ratio, and in G-lignin, it was correlated with p-hydroxyphenyl content.

2006-P26

アルカリ及びアルカリ酸素処理において α-カルボニル基の存在が及ぼすリグニン分解反応への影響

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Effects of the presence of α-carbonyl group on the degradation reactions of lignin during anaerobic and aerobic alkaline treatments

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Abstract: It is well known that the presence of α-carbonyl group in lignin has a significant effect on its reactivity toward various chemical reactions. However in most of the researches, the effect has been studied when α-carbonyl group is located at the lignin phenylpropane unit where the target reactions are occurred (located at A-ring). In this study, the effect of α-carbonyl group on the reactions occurred under anaerobic and aerobic alkaline conditions was examined when the group is located at the unit next to that where the reactions are operative (located at B-ring) using a dimeric lignin model compound, guaiacylglycerol-β-ethylvanillin ether (GE). A significant amount of ethylvanillin was obtained in the nitrogen-alkali treatment of GE. This result indicates that the presence of α-carbonyl group at the B-ring surprisingly accelerates the alkali promoted β-O-4 bond cleavage. A large amount of vanillin was obtained in the oxygen-alkali treatment of GE. This is quite contrast to the result observed when an analogous model compound of GE without the α-carbonyl group was treated under the same conditions. These phenomena indicate that the rate of the Cα-Cβbond cleavage exceeds that of the aromatic ring scission. It is suggested that the presence of α-carbonyl group at the B-ring changes the reaction site of lignin where oxygen oxidation is occurred.

2006-P27

ケナフリグニンの化学構造について

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Chemical structures of kenaf (*Hibiscus cannabinus*) lignin

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Abstract: Kenaf (*Hibiscus cannabinus*), variety Everlglades, bast native and isolated lignins were subjected to analytical pyrolysis to confirm unusual structures of kenaf lignin. Pyrolysis results showed that the kenaf sample employed in the present study contains no comiferyl and sinapyl alcohols with an acetyl group at the γ-position, and it has a paucity of 5-hydroxyguaiacyl units because the small abundance of 3-methoxycatechols was present in the pyrolyzates.

2006-P28

ケナフ靭皮クラフトパルプの酸素漂白特性

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Characteristic of kenaf bast kraft pulp for oxygen bleaching

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Abstract: Kraft cooking efficiency of bast of *Hibiscus cannabinus* (kenaf) was compared with that of *Acacia mearnsii* and *Eucalyptus* spp. Although the lignin content of the bast was lower than that of *A. mearnsii* wood, the selectivity of delignification of the bast was not better than that of the hardwoods. The bast contained more uronic acids than the hardwoods. Then, it consumed more alkali during kraft cooking and did not show better delignification selectivity. However, the bast pulp was easily oxygen-bleached at a small alkali charge,

resulting in a low kappa number.

2006-P29

リグニンの温度変調型 DSC 分析

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Temperature modulated DSC analysis of isolated lignin

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Abstract: DSC is commonly used to examine the thermal properties of lignin preparations. However, in many of the lignin preparations a large enthalpic relaxation peak overlaps the glass transition, Tg, region in the DSC curve, which makes it difficult to identify the Tg. This is typically addressed by applying a pre-heat treatment (first scan) to remove this endothermic peak. However, lignin preparations have thermosetting properties as well as thermo-plasticity; the chemical structure of lignin changes during the heat treatment. To avoid this problem, temperature modulated DSC (TMDSC) was examined for thermal analysis of lignin preparation. By use of TMDSC, an enthalpic relaxation peak can be removed from total heat flow, and Tg of lignin preparation can be clearly seen without pre-treatment, In conventional DSC run, Tg temperature of lignin preparations were only slightly increased by repeating heat treatment. However, Tg temperature measured in 2nd heating run is remarkably higher than in 1st heating. This indicates that pre-heat treatment of DSC run affects the Tg of the lignin preparation.

2006-P30

β–*O*–4 型人工リグニンポリマーの合成とその性質　–シリンギルタイプの合成–

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Synthesis of β–*O*-4 type artificial lignin polymers and their properties - Synthesis of syringyl type lignin polymer -

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Abstract: The β-*O*-4 structure is one of the most important substructures in lignin. Guaiacyl type artificial lignin polymer composed of only β-*O*-4 structure has been synthesized in our laboratory. In this investigation syringyl type monomer was treated with potassium carbonate and reduced with sodium borohydride to yield a polymer. The polymer was acetylated and fully analyzed by NMR spectroscopy.

2006-P31

オルガノソルブリグニンアルキルエステル／ポリ（ε-カプロラクトン）環境適合型ブレンドの相構造評価

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Phase structure of biodegradable poly(ε-caprolactone) with organosolv lignin alkyl esters

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Abstract: Organosolv lignin (OSL) alkyl esters (carbon number, 2-5) were synthesized by a homogeneous reaction with different acyl anhydrides/4-dimethylamino pyridine in pyridine solution. The miscibility of the esterified OSLs with poly(ε-caprolactone) (PCL) was investigated, mainly through thermal analysis by differential scanning calorimetry (DSC). DSC analysis revealed that a polymer pair OSL butyrate/PCL and valerate/PCL showed a compatibility. Atomic force microscopy also indicated that no remarkable phase separation occurred in these two blends.

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2007-101

ゼラチン層を形成しない広葉樹あて材におけるリグニン分布

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Lignin distribution in tension wood cell walls without gelatinous layer

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Abstract: The present study investigated affects of inclination angle on reaction wood formation in three angiosperm species (*Paulownia tomentosa*, *Liriodendron tuliplfera*, and *Osmanthus fragrans*) which do not form typical gelatinous fibers. These sample trees were inclined artificially at angle of 30, 50, 70 degrees from the vertical. The amount of lignins was decreased by tension wood formation in the intercellular layer and wood fiber walls. It was found that inclination angle affects the amount of syringyl unit in lignins.

2007-102

ToF−SIMS による広葉樹木部におけるリグニン分布の解析

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Lignin distribution in the cell walls of angiosperm xylem determined by ToF-SIMS

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Abstract: Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used to investigate the heterogeneous distribution of guaiacyl and syringyl lignin in the transverse section of the xylem of *Acer micranthum*. The lignin distribution was visualized by ToF-SIMS direct mapping of secondary ions with guaiacyl or syringyl rings at m/z 137 and m/z 167, respectively. The result supports the previous observation obtained by Mäule color reaction that the vessels are rich in guaiacyl lignin and the fibers are rich in syringyl lignin.

2007-103

ポプラペルオキシダーゼの遺伝子およびタンパク構造の多様性

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Structural diversity of poplar peroxidases

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Plant peroxidases form a numerous multigenic family in higher plants. We have surveyed peroxidase genes in the *Populus trjchocarpa* database and found at least 79 sequences encode complete peroxidase protein with manual anotation, and diversity of peroxidase isoenzymes was investigated from genome structure and amino acid sequences. The coding sequence of the majority of the peroxidase genes are disrupted by three introns. The genes excluding this structure bring some light on the evolutionary steps encountered during the diversification of poplar peroxidase genes. Within the protein structure of 79 putative peroxidases, observed changes of highly conserved residue may cause significant change in enzyme kinetics and functions, and this observation suggest the diversification of plant peroxidases.

2007-104

改変型植物酸性 peroxidase の酵母での発現と精製

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Heterogeneous expression and purification of modified plant peroxidase
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Abstract: PrxA3a is an anionic peroxidase from hybrid aspen. A gene, *prxA3a*, was fused with sequence of His-tag. The construct was inserted into the downstream of FLAG sequence in a yeast expression vector, YEpFLAG. Active peroxidase was secreted into the medium. The secreted peroxidase was purified by Ni-column. The peroxidase might be highly glycosylated. Other modified peroxidase is also analyzed.

2007-105
リグニン生合成を抑制した飼料用・エタノール変換用イネの分子育種
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Down regulation of cinnamyl alcohol dehydrogenase (CAD) induces increase of cell wall digestibility in rice (*Oryza sativa*)
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Abstract: Cinnamyl alcohol dehydrogenase (CAD) is the enzyme of the lignin-specific biosynthesis. Inverted repeats constructs of the DNA encoding CAD of *Oryza sativa* have been introduced into rice plants. CAD down-regulated plants did not displayed any abnormal phenotype compared with a wild type. Lignin content and cell wall digestibility measurement was performed on the transformants. Lignin content was not reduced, but cell wall digestibility increased. This suggested CAD down-regulation induced change in lignin composition. As a result, increasing of cell wall digestibility without weakening plant structure is realized.

2007-106
モノリグノール配糖体によるシリンギル型 DHP の生成挙動の解析
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In-situ UV spectroscopic study on the horseradish peroxidase-catalyzed polymerizations of monolignol glycosides
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Abstract: Horseradish peroxidase catalyzed homopolymerizations of syringyl-type (S-type) glycoside **1S** and copolymerizations of **1S** with guaiacyl-type (G-type) glycoside **1G** were monitored by *in situ* UV spectroscopy. In the former, new absorption peak at 325 nm (A_{325}) from S-type quinone methide intermediates (S-QM) increased rapidly within 30 min, and then disappeared gradually, suggesting that the reactivities of the S-QM are significantly low. In the latter, the addition of **1G** promoted both of the increase and the following decrease of A_{325}, suggesting that **1G** acts not only as a radical mediator but also as a nucleophile for the S-QM during the copolymerizations.

2007-107
担子菌のラッカーゼ遺伝子を導入した組換え植物が示す雄性不稔の解析
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Analysis of male sterility in transgenic plants with the chimeric gene for fungal laccase
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2007-108
イネをモデル植物とした細胞壁形成過程に関する研究 −Glycosylphosphatidylinositol-anchored protein はイネの細胞壁高次構造形成にどのように関わるのか？(3)ー

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Study of plant cell wall formation in *Oryza sativa* L. -How does glycosylphosphatidylinositol- anchored protein relate fo cell wall conformation in rice plant (Oryza sativa L.) ? (3)-

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Abstract: To understand the mechanism that regulate the high-order conformation of plant cell wall, a mutant defective in stem strength had been isolated and characterized. A rice mutant *cell wall architecture 1* (*cwa1*) exhibits the systemic brittle-culm phenotype with indistinguishable morphology from wild-type plant. Whereas abnormal depositions that contain much phenols were found at secondary cell wall in cortical fiber regions of *cwa1*. Thus *cwa1* is likely to be defective in control of cell wall architecture but not in biosynthesis of cell wall. We suggest that defective protein of *cwa1*;BC1 work as a scaffold for precise localization of each cell wall components.

2007-109

ヤマモモ抽出成分ミリカノールの生合成、 –*p*–クマール酸および *p*-ヒドロキシフェニルプロパン酸の投与とその取り込み–

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Myricanol biosynthesis in *Myrica rubra* - Feeding experiments of *p*-coumaric acid and *p*-hydroxyphenylpropanoic acid -

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Abstract: Diarylheptanoids are one of the major wood extractives and have C_6-C_7-C_6 carbon skeleton. However, there is little evidence about the biosynthetic pathways for diarylheptanoids. We have investigated the biosynthesis of cyclic diarylheptanoid myricanol, which is the major extractive in *Myrica rubra*, and previously reported *in vivo* feeding experiments using [β, γ-$^{13}C_2$]-*p*-coumaric acid. The results indicated that the involvement of two molecules of p-coumaric acid for myricanol biosynthesis in *M. rubra*. In the present study, we reports that the assignments of the incorporated positions of [β, γ-$^{13}C_2$]-*p*-coumaric acid into myricanol with ^{13}C-NMR studies. Furthermore, to clarify whether *p*-hydroxyphenylpropanoic acid is a precursor for myricanol biosynthesis, ^{13}C-labeled *p*-hydroxyphenylpropanoic acid was prepared and administrated into *M. rubra*. The results reveal that [γ-^{13}C]-*p*-hydroxyphenylpropanoic acid is incorporated into myricanol.

2007-110

Isolation of *Anthriscus sylvestris* *O*-methyltransferase cDNAs

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Abstract: In order to further understand the role of *O*-methyltransferases (OMTs) in podophyllotoxin biosynthesis, we have isolated 7 OMT cDNAs from an *Anthriscus sylvestris* cDNA library. The isolation using digoxigenin (DIG) labeled probes resulted in 62 positives and further screening narrowed them down into 7 cDNA clones. Phylogenetic analysis showed that the 7 cDNA clones have high identity towards their respective probes. Among the isolated clones, we are particularly interested in clone #50 due to its close phylogenetic relationship with AEOMT. The clone is predicted to encode an AEOMT-like protein, which has a similar role in plant metabolism. Expression and characterization of the 7 clones are currently underway.

2007-111

白色腐朽菌 *Phanerochaete sordida* YK-624 株の形質転換系構築及び新規リグニンペルオキシダーゼの発現

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Homologues expression of novel lignin peroxidases in *Phanerochaete sordida* YK-624

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Abstract] In our previous reports, the gene transformation system of white-rot fungus *Phanerochaete sordida* YK-624 has been developed, and we have cloned two cDNAs (*ylpA* and *ylpB*) and two genomic DNAs (*g-ylpA* and *g-ylpB*) encoding YK-Lips which are novel lignin peroxidases from this fungus. In the present study, we tried homologues expression of YK-Lips. The glyceraldehyde-3-phosphate dehydrogenase (GPD) promoter was used to drive the expression of *g-ylpA* or *g-ylpB*, and plasmids (pGPD-*g-ylpA* and pGPD-*g-ylpB*) were constructed. Transformants were screened for YK-Lip activity in the liquid cultures (1.2 mM ammonium tartrate, pH 4.5), and A-11 and B-3 were selected as transformants which were high YK-Lips-expressing strains. Recombinant YK-Lips were secreted in active form by these transformants after 4 days of growth, whereas endogenous YK-Lips genes were not expressed in manganese-deficient liquid culture (40 mM ammonium tartrate, pH 6.5).

2007-112

シキミ酸経路を経由したグルコースからの 2-pyrone4, 6-dicarboxylicacid の発酵生産

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Biological conversion of glucose to 2-pyrone-4, 6-dicarboxylic acid by the bypassed shikimate pathways

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Abstract: PDC, 2-pyrone-4, 6-dicarboxylic acid, is one of metabolic intermediates in *Sphingomonas paucimobilis* SYK-6 that is a degrader of lignin-derived compounds. PDC has been characterized as a material for synthetic polymers. In the previous study, we have already constructed the system on which PDC was efficiently converted from vanillic acid and vanillin. In order to develop alternative system for PDC production, we try to produce it from glucose, which is one of low-cost sugars expected to be converted from abundant cellulose wastes and biomass crops. In the present study, we generated six types of recombinant bacteria. PDC could be produced from glucose by all of the bacteria analyzed. Especially, the recombinant bacteria with *qutC* could produce PDC at high concentration than those with *ubiC* and *pobA*. Our results suggest that *qutC* is useful gene for the fermentative production of PDC.

2007-113

Biodegradation of chrysene in a soil by fungi screened from nature

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Abstract: *Polyporus* sp. S133, a fungus collected from soil, was selected for its ability to grow on and degrade chrysene as a sole carbon source. The effect of adding several concentrations of tween 80 to increase degradation rate of chrysene was studied. Maximal degradation (86%) was obtained when *Polyporus* sp. S133 was incubated in a soil supplemented with 0.50% of tween 80. The mechanism for degradation of chrysene with the fungus through identification of the intermediates was found. Several enzymes (manganese peroxidase, lignin peroxidase, laccase, 1,2-dioxygenase and 2,3-dioxygenase) produced by *Polyporus* sp. S133 were detected in the culture. The highest enzyme activity was shown by 1,2-dioxygenase after 20 days of cultivation (237.5 UI^{-1}). Those ligninolytic and dioxygenase enzymes played an important role to oxidize chrysene.

2007-114

Degradation of 1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane (DDT) by brown rot fungus *Fomitopsis pinicola*

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Abstract: Fomitopsis *pinicola* showed high ability to degrade DDT in PDB medium. To investigate the involvement of Fenton reaction, mineral salt medium with or without $FeSO_4$ was used. *F. pinicola* showed higher ability to degrade DDT in medium without $FeSO_4$ than that in medium with $FeSO_4$ either in vivo or in vitro experiment. It indicates that the extracellular iron-dependent reaction was not involved in DDT degradation by *F. pinicola*. DDD (1,1-dichloro-2,2-bis(4- chlorophenyl) ethane) was detected as metabolic product from DDT degradation. The transformation of DDT to DDD by *F. pinicola* might be involved extracellular enzymatic reaction.

2007-115

耐塩性白色腐朽菌 *Phlebia* sp. MG60 におけるペルオキシダーゼ転写制御

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Transcriptional regulation of manganese peroxidases from saline–tolerant white rot fungus, *Phlebia* sp. MG60

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Abstract: The expression pattern of manganese peroxidases (MnPs) in nitrogen-limited cultures of saline-tolerant fungus, *Phlebia* sp. MG-60, is differentially regulated under a hyper-saline condition at the transcriptional level. When MG-60 was cultured in the nitrogen limited medium containing 3% sea salts (LN-SSM), higher activity of MnPs was observed than that in the normal medium (LNM). SDS-PAGE analysis demonstrated that two MnP isoenzymes were de DOVO synthesized during the culture in LN-SSM. Three MnP encoding genes (*MG-mnp1*, *MG-mnp2*, and *MG-mnp3*) were isolated by RT-PCR and RACE-PCR techniques, and identification of each MnP protein was achieved by peptide mass fingerprinting (PMF) analysis of the tryptic fragments of each MnP isoenzyme observed on SDS-PAGE. Two MnP isoenzymes that were mainly observed in LN-SSM were encoded by *MG-mnp2* and *MG-mnp3*. Real-time PCR analysis revealed that *MG-mnp2* and *MG-mnp3* were highly transcribed in LN-SSM, and the transcription was induced 48 h after the addition of 2% NaCl. The induction of MnP production and gene transcription by saline was well correlated in the presence of Mn^{2+}. However, in the absence of Mn^{2+} there is no clear correlation between *mnp* transcription and MnP activity, suggesting the existence of a post-transcriptional regulation by Mn^{2+}.

2007-116

Phanerochaete chrysosporium のリグニン分解能を支える代謝制御機構

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Systems biology of lignin biodegradation

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Abstract: Effect of exogenous vanillin on a cellular system in *Phanerochaete chrysosporium* was investigated utilizing integrative OMICS. Addition of vanillin caused an immediate flux shift at the TCA cycle, initiating a production of succinyl CoA. Transcriptomic data obtained from a 50-mer oligoDNA microarray system combined with proteomic data clearly indicated the activation of the heme biosynthetic pathway branched at succinyl CoA. Up-regulation of extracellular peroxidases and several cytochrome P450s was also observed. Addition of vanillin also brought about a down- regulation of extracellular oxalate dehydrogenase and intracellular formate dehydrogenase and an up-regulation of enzymes in mannitol cycle, suggesting the presence of unique regulation system for energy production in the fungus. These metabolic shifts seem to be required for optimizing its ligninolytic system.

2007-117

フリーラジカルによるリグニンモデル化合物の反応部位に関する研究

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Study on reactive position of lignin model compounds with free radicals

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Abstract: A white rot fungus, *Ceriporiopsis subvermispora* degrades lignin by radical reactions of low molecular mass metabolites at a site far from enzymes. As a possible ligninolytic system by the fungus, *in situ* radical reactions have been proposed. In the degradation of non-phenolic lignin model compounds (LMCs) by free radicals, it was proposed that the reaction was initiated by hydrogen Abstraction from the benzyl position of LMCs. However, no concrete evidence has been presented. In the present study LMCs were reacted with *tert*-butoxyl radical generated by UV-photolysis of di-*tert*-butyl peroxide, and radical intermediates from the LMCs were analyzed by ESR. Reactivity of free radicals with the LMCs was also analyzed using *ab initio* MO calculation.

2007-特別講演 I

ブラシノステロイド研究の始まりと現在の進展

横田孝雄
帝京大学理工学部バイオサイエンス学科

2007-201

リグニン熱分解物の気相における二次熱分解反応

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Secondary reactions of lignin-derived pyrolysis vapor

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Abstract: Secondary reaction of lignin-derived primary tar (guaiacols with various side-chain) in vapor phase was studied with milled wood lignin (from Japanese cedar: *Cryptomeria japonica*) and various model compounds (conditions: N_2/600 ºC/ 50-120 s). The benzene-ring and side-chain structures were found to change in the following pathways: benzene-ring: guaiacyl- → catechol-, *o*-cresol (2-methylphenol)- and phenol-types, side-chain: >C=C<, -CHO and >C=O → -H and saturated alkyl chain types. Secondary carbonization was also observed during these structural changes of the tar components, especially disappearing the $-OCH_3$ groups. These results indicate that the secondary carbonization is closely related to the formation of phenoxy and methyl radicals through the $O-CH_3$ bond homolysis. This is also supported by the experimental fact that only the model compounds with aromatic $-OCH_3$ formed secondary char.

2007-202

リグニン β−エーテル構造の熱分解ラジカル連鎖開裂反応

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Radical chain mechanisms in pyrolytic β-ether cleavage suggested from the products of lignin model dimers and trimer

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Abstract: Pyrolysis of lignin model dimers (phenolic and nonphenolic β-ether type) and trimer (nonphenolicα, β-ether type) in a closed ample (N_2) at 400ºC for 2min gave Cα=O and isoeugenol (Cα=Cβ) types products as the β-ether-cleavaged products. Formation of these products indicates that radical chain reactions proceed through H-Abstraction of the Cα-H and phenolic-OH.

2007-203

全細胞壁の溶液 NMR 法によるイチョウのプロトリグニンの ^{13}C 標識2D−NMR 示差スペクトル分析

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2D-NMR difference spectra between specifically ^{13}C-enriched and unenriched ginkgo protolignin by solution-state whole-cell wall NMR

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Abstract: Coniferins specifically ^{13}C-enriched at side chain carbons and unenriched coniferin were administered to growing stems of ginkgo. The whole newly formed xylems containing ^{13}C-enriched and unenriched lignins were milled and dissolved in a mixture of N-methylimidazole and DMSO, then acetylated. Solution-state 2D-NMR (HSQC) spectra of the dissolved whole xylem cell walls were determined in high resolution. Determination of difference spectra between the spectra of whole cell walls containing ^{13}C-enriched and unenriched lignins afforded simplified 2D spectra in which all signals were assigned exclusively to the specifically enriched carbons. The present novel NMR technique provides a useful nondestructive tool for elucidation of the structure and behavior of entire lignin in the cell wall (protolignin) not only in ginkgo but also in most common conifers.

2007-204

構造を制御した人工リグニンの化学合成

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Synthesis of β-O-4 type artificial lignin polymers

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Abstract: The β-O-4 structure is one of the most important substructures in lignin. Artificial lignin polymer composed of only β-O-4 structure has been synthesized in our laboratory. Brominated acetophenone derivatives were treated with potassium carbonate and reduced with sodium borohydride to yield polymers. The polymers were acetylated and fully analyzed by NMR spectroscopy. The spectra of guaiacyl-type homopolymer and guaiacyl/syringyl-type heteropolymer with three-carbon side chain were well consistent with β-O-4 substructure in milled wood lignin from Japanese tdo fir wood and Japanese white birch wood, respectively.

2007-205

β-*O*–4 結合定量法としてのチオアシドリシス法の評価、−β-*O*-4 型人工リグニンポリマーの反応の定量性から–

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Thioacidolysis as quantitative determination of β-*O*-4 bond -Quantifiability of the reaction of β-*O*-4 type artificial lignin polymer-

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Abstract: Thioacidolysis is a method for quantitative determination of β-*O*-4 bond in lignin. We established the synthetic route to artificial lignin polymer comprised of only β-*O*-4 linkage. In this study, we evaluated thioacidolysis reactivity to β-*O*-4 bond by using this lignin polymer. The monomer yield for the artificial lignin polymer was less than 100% (about 70%) under the conventional thioacidolysis conditions, whereas approximately 100% yield for the dimer model compound under the same conditions. No enhancement of monomer yield was observed, by prolonging reaction time. These results suggest that thioacidolysis was not a stoichiometrical decomposition method for β-*O*-4 macromolecule.

2007-206

リグニンおよび微生物変性水可溶リグニンの超臨界水・亜臨界水条件下での反応：原油生成機構

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Reaction of lignin and biologically modified lignin under supercritical and subcritical water conditions:

Presumptive production mechanism of petroleum

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Abstract: The annual discharge of dissolved organic mater (DOM) and particulate organic matter (POM) from rivers to ocean is estimated as ~0.4 x 10^9 ton, which are primarily composed of biologically modified remains of terrestrial vegetation. The DOM in the ocean could form insoluble sediments by chelating with metal ions and considered to be precursor of kerogen. Kerogen is defined as the sedimentary organic matter generating petroleum, which is an insoluble matter, in contrast petroleum soluble in usual organic solvents. Reaction of model compounds, Björkman lignins and DOM were examined under supercritical water condition to confirm the formation mechanism of petroleum at deep sea, where is subcritical condition. It was confirmed that demethylation and demethoxylation reactions were the major reactions of lignins and DOM. These reactions also were confirmed by phenol, guaiacol and 2,6-dimethoxyphenol (syringol) as model compounds.

2007-207

ハード酸とソフト塩基の組み合わせによるリグニンエーテル結合の新規開裂方法の検討

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A novel ethereal bond cleavage of lignin interunit linkage by a combination of hard acid and soft base

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Abstract: Ethereal bond cleavage of wood meal, isolated lignin, and lignin model compound (guaiacylglycerol-β-guaiacyl ether) by aluminium (III) iodide, known as a hard Lewis acid as well as a soft nucleophile, were investigated to explore a new procedure to delignify woody preparations effectively under relatively mild reaction conditions. The lignin model compound was successfully degraded even when treated at room temperature for 4.5 hours, suggesting AlI_3 can cleave ethereal bond of lignin structural units under some mild reaction conditions. Enhanced delignification of wood meal by AlI_3 treatment at refluxing temperature was also observed, but optimized conditions were yet to be established.

2007-208

炭水化物のアノマー位に対する活性酸素種の反応性の評価

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Evaluation of the reactivity of active oxygen species toward the anomeric position of carbohydrate

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Abstract: The reactivity of active oxygen species (AOS) toward two different anomeric types of carbohydrate was examined using methyl α-D-glucopyranoside (MGPα) and methyl β-D-gluco- pyranoside (MGPβ). In this study, AOS were in situ generated by subjecting a phenolic compound, 2,4,6-trimethylphenol (TMPh), to the oxygen oxidation. As the degradation of MGPβwas greater than MGPα, it was suggested that the stereo configurational difference in their anomeric positions has an influence on their reactions with AOS. It was also examined whether or not the anomeric position is certainly attacked by AOS subjecting TMPh, MGPβ, and methyl β-D-[1-d]-gluco- pyranoside (MGPβ[1-d]) to the oxygen oxidation. The result obtained by the GC-MS analysis showed that the degradation of MGPβ[1-d] is slower than MGPβsuggesting a possible occurrence of the certain Abstraction of the anomeric hydrogen.

2007-209

酸性下におけるリグニン β-O-4 結合開裂機構の再評価 (4) 一酸の種類の影響について一

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Reevaluation of the mechanism for the cleavage of lignin β-O-4 bond under acidic conditions (4)

—On the effect of kind of acid—

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Abstract: A dimeric non-phenolic lignin model compound, veratrylglycerol-β-guaiacyl ether (VG), was treated with HBr in 82% aqueous dioxane. It was found that the elimination of γ-position as formaldehyde does not occur in the system. Because the C_6-C_3 type enol ether afforded from VG by the water elimination was not detected at all, it could not be clarified whether or not the enol ether is produced during die VG acidolysis. The results obtained by the use of VG with the deuterium at the β-position (VG_{bD}) indicated that the Abstraction of the β-proton from the benzyl cation structure resulting in the formation of the C_6-C_3 type enol ether (referred to reaction (I) in the following) probably relates to the rate-determining step in the disappearance of VG. However, because the difference in die β-O-4 bond cleavage rate between kind of acids cannot be explained from the rate difference in die reaction (I), there seems to be another step with a similar rate to the reaction (I), where kind of acids affects its rate.

2007-210

国産針葉樹材アルカリパルプのヘキセンウロン酸含有量と無塩素漂白特性

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Hexenuronic acid contents of various alkali pulps from Japanese softwood and their non-chlorine bleaching response

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Abstract: We estimated hexenuronic acid (HexA) contents and lignin contents of various alkali pulps given by kraft, kraft-anthraquinone (kraft-AQ), and polysulfide-anthraquinone (PS-AQ) cookings based on some cooking factors such as cooking time, active alkali charge, AQ charge, and sulfur charge. HexA contents of PS-AQ and kraft-AQ pulps with kappa number 25 at H-factor 1200 from Japanese softwood were higher than that of the conventional kraft pulp. Various alkali pulps were bleached using the O-A-Z-E-Ep sequence. We discussed that their non-chlorine bleaching response from the standpoint of brightness and residual HexA contents.

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南アフリカ産ユーカリ材のクラフト・アントラキノン蒸解および無塩素漂白特性

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Characteristics of various eucalyptus woods from South Africa for kraft-AQ cooking and TCF bleaching

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Abstract: *Eucalyptus nitens*, *E. grandis*, *E. smithii* and *E. macarthurii* woods grown in South Africa, which have been used in Japanese pulp mills, were investigated to clarify their characteristics for kraft-anthraquinone (AQ) cooking and totally chlorine-free (TCF) bleaching. They had various densities from 0.477 to 0.751 g/cm^3. Lower lignin contents on original wood resulted in higher pulp yields. Higher ratios of syringaldehyde to vanillin by alkaline nitrobenzene oxidation of lignin brought higher brightness after cooking. After oxygen bleaching, the kappa number decrease of *E. grandis* pulp was quite low because of its high hexenuronic acid content which contributed kappa number. Pulp sheet were made under neutral conditions after TCF bleaching and the accelerated yellowing tests were performed. Each pulp showed little brightness reversion, and there are no clear relationship between the hexenuronic acid (HexA) contents and the brightness reversion. All TCF bleached pulps except *E. grandis* showed high brightness around 85% ISO and *E. smithii* is the highest (86.7% ISO).

2007-212

アルカリ処理オゾン酸化リグニンのアルミニウム毒性除去能についての研究

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Studies on elimination of aluminum toxicity with modified kraft lignin

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Abstract: Ozone treated kraft lignins were subjected to alkaline treatment and the effect of these modified kraft lignins on elimination of aluminum toxicity was assayed by planting experiment. Modified kraft lignins with ozone followed by alkaline treatments were more effective on elimination of aluminum toxicity and acceleration of root growth than that with only ozone. It is, furthermore, observed that the kraft lignin which was subjected to alkaline treatment was also effective on elimination of aluminum toxicity and acceleration of root growth in this experiment. This fact suggests that kraft lignin itself has chemical structure which is effective on above favorable effects.

2007-213

リグノスルフォン酸塩ー糖蜜系木質充填型バイオコンポジットの熱的・機械的性質

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Thermal and mechanical properties of sodium lignosulfonate and molasses-based polyurethane biocomposites

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Abstract: Molasses (ML) is obtained as a by-product of the sugar industry. Sodium lignosulfonate (LS) is obtained as a by-product of the pulping industry. ML polyol (MLD) and LS polyo1 (LSD) are obtained by dissolving ML and LS in diethyleneglycol (DEG). In this study, MLD and LSD were reacted with poly(phenylene methylene) polyisocyanate MDI) that was used for the preparation of molasses- and lignin-based polyurethane (PU) composites using wood meal as fillers. In the above biocomposites, wood meal contents were changed from 50 to 90 %. MLD and LSD mixing ratios were changed as follows, 0:100, 20:80, 40:60, 50:50, 60:40, 80:20, 100:0. Apparent density, compression and thermal properties of the PU composites were examined. Apparent density and compression strength showed the optimum point at MLD and LSD the mixing ratio 60:40. Thermal degradations (T_d) of composites were observed as two steps, low temperature side (T_{d1}) and high temperature side of thermal degradation (T_{d2}). The T_{d1} at ca. 290ºC is attributed to the degradation of MLPU and LSPU matrix. The T_{d2} observed at 310-360ºC is attributed to the degradation of wood meal. It was found that mechanical and thermal properties of composites are controllable through reaction conditions.

2007-214

リグニンスルホン酸塩を原料とする飽和及び不飽和エステル型エポキシ樹脂の合成と熱的性質

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Synthesis and thermal properties of epoxy resins with saturated and unsaturated ester chains from ligninsulfonate salt

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Abstract: Sodium ligninsulfonate (LS) was dissolved in ethylene glycol (EG) and the obtained mixture was allowed to react with succinic anhydride to form a mixture of ester-carboxylic acid derivatives (LS-EG polyacid, LSEGPA). EG-polyacid (EGPA) was also prepared from EG. The mixture of LSEGPA and EGPA was reacted with ethylene glycol diglycidyl ether in the presence of catalytic amount of dimethylbenzylamine to form epoxy resins. The molar ratio of epoxy groups to carboxylic acid groups ([EPOXY]/[AA] ratios, mol/mol) was maintained at 1.1. The contents of LSEGPA in the mixture of LSEGPA and EGPA (LSEGPA content) were varied from 0 to 100%. A mixture of ester-carboxylic acid derivatives (LS-EGM polyacid, LSEGMPA) and EGM-polyacid (EGMPA) were also synthesized using maleic anhydride. Thermal properties of epoxy resins were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG). Glass transition temperatures (T_g's) of epoxy resins increased with increasing LSEGPA and LSEGMPA contents suggesting that lignin acts as a hard segment in epoxy resin networks. Thermal decomposition temperatures (T_d's) of epoxy resins were almost constant regardless of LSEGPA and LSEGMPA contents.

2007-215

オルガノソルブリグニンアルキルエステル／ポリ（□ーカプロラクトン）相溶ブレンドの相構造評価と結晶化挙動

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Phase structure and crystallization behavior of biodegradable blends of poly(□-caprolactone) with organosolv lignin alkyl esters

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Abstract: Organosolv lignin (OSL) alkyl esters (carbon number, 2-5) were synthesized by a homogeneous reaction with different acyl anhydrides/4-dimethylamino pyridine in pyridine solution. The miscibility of the esterified OSLs with poly(□-caprolactone) (PCL) was investigated, mainly through the evaluation of the glass transition temperature (T_g) using differential scanning calorimetry (DSC). DSC analysis revealed that the blends of OSL esters with n=3-5 with PCL showed a composition-dependent shift in T_g. Therefore, the blend systems can be regarded as miscible ones in a scale of T_g-detection, usually assumed to be less than a couple of tens of nanometers. Atomic force microscopy also indicated that no remarkable phase separation occurred in these blends. On the other hand, it was noted that the crystallinity of PCL vanished for PCL-rich compositions of the miscible pairs. This observation also supports that the blends show the higher degree of miscibility with PCL. In order to obtain further details of the crystalline development, isothermal crystallization experiments were conducted by means of polarized optical microscopy.

2007-216

イオン液体への木材の溶解性とリグニンモデル化合物の安定性

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Solubility of wood and stability of lignin model compounds in ionic liquid

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Abstract: Structure stability of lignin model compounds in ionic liquids was studied to develop the novel isolation methods of lignin and LCC from wood. Four imidazolium based ionic liquids, and two phenolic lignin model compounds, Guaiacy1glycerol-β-guaiacyl ether and its α- ethoxy model compound, were examined in this study. Under the temperature condition of 120 ºC, cellulose component in wood meal were decrystalized by more than 48 hs treatment. However, lignin model compounds were gradually decomposed under this temperature condition with extending the processing time. Depending on the ionic liquid used, more than 40% of loaded model compound were decomposed for 48 hs treatment. Under the lower temperature condition (100 ºC), those model compounds were relatively stable. Decomposition degree after 48 hs treatment was less than 20% in chlorinated ionic liquid, 1-Butyl-3-methylimidazolium and 1-Allyl-3-methylimidazolium chloride, although significant decomposition was estimated in other ionic liquids.

2007-特別講演 II

熱分解ガスクロマトグラフィーによるリグニンの分析

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Invited Lecture, II: Analysis of lignin by pyrolysis-gas chromatography

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Abstract: Emergence of analytical pyrolysis combined with modern instruments such as gas chromatography and/or mass spectrometry has provided new possibilities to analyze the lignin owing to its high sensitivity, lesser sample-preparation steps and a short analysis time. Under controlled pyrolysis conditions, lignin is reproducibly broken to give products retaining structural attributes. This paper examines several recent advances in analytical pyrolysis. Selected aspects are exemplified using original results.

2007-P01

イネ稈及び葉鞘の組織構造とリグニン分布

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Anatomy and lignin distribution of stem and leaf tissues in *Oryza sativa*

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Abstract: For utilization of biomass resources, anatomy and lignin distribution of stem and leaf tissues in *Oryza sativa*, which is one of the popular crops in Japan, were investigated. Tracheid wall and vessel walls in vascular bundles in cortex and parenchyma tissues showed pinkish color after Wiesner reaction. Spectrophotometry analysis showed a distinct absorption peak around 570 nm in these walls after Wiesner reaction, suggesting that substances with coniferyl aldehyde structure exist in these tissues. On the other hand, fiber walls in cortex were weakly stained with Wiesner reagent and did not show any distinct peak in visible-light absorption microspectra. These results indicate that the amount and type of lignin in cell walls of *O. sativa* vary among cell types.

2007-P02

Lignin deposition and peroxidase activity in Japanese birch plantlets (Tohoku) infected with *lnonotus* obliquus IO-U1 strain

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Abstract: Histochemical studies were undertaken on defensive reactions of *Betula platyphylla* var. *japonica* Tohoku clone after infection with *Inonotus obliquus* IO-U1 strain. As a defensive reaction, phenolics deposition was found rapidly within 2 hrs of infection and reached extensive by 10 days. The peroxidase activities were observed in phenolics-deposited cell walls. Cell walls of vessels and wood fibers were rich in lignin at the infection site in 10 days of treatment. These histochemical changes are considered to occur as defense reactions in the infected Tohoku birch plantlets.

2007-P03

モノリグノール類の電解重合

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Electropolymerization of monolignols

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Abstract: We carried out anodic oxidation of monolignols, especially coniferyl alcohol, by galvano-static (constant-current) method. Using dichloromethane/methanol as a mixed solvent, a yellow filmy product was deposited on Pt anode during the electrolysis reaction. Although the yield of this electropolymerized product was very low, thioacidolysis analysis suggests that it has high β-O-4 linkage content. Probably, the electropolymerization of monolignols could produce the characteristic polymer that we have not obtained from conventional DHP preparation method.

2007-P04

リグニン重合機構の解明 −モノリグノールのラジカル重合の可能性−

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Elucidation of the lignin polymerization mechanism -Possibility of radical polymerization of monolignol-

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Abstract: We investigated possibility of radical polymerization of coniferyl alcohol as a monolignol. The monolignol was found to be polymerized under the solution polymerization conditions with and without initiators. The resultant polymeric materials contain aliphatic alcohols having only a few double bonds. These results suggest that the polymer was formed by radical polymerization together with dehydration.

2007-P05

ポプラペルオキシダーゼアイソザイム CWPO–C の機能解析

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Function of cationic cell-wall-peroxidase (CWPO-C) from poplar

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Abstract: A unique peroxidase isoenzyme, cationic cell-wall-peroxidase (CWPO-C), from poplar oxidizes sinapyl alcohol, ferrocytochrome *c* and synthetic lignin polymers, unlike other plant peroxidase. Recently, catalytic mechanism of CWPO-C was investigated using chemical modification and homology modeling. It was suggested that Tyr residues on the protein surface, such as Tyr-177 and Tyr-74, are considered to be important for the oxidation activities of CWPO-C with a wide range of substrates. In this study, we focused on CWPO-C homolog genes of *Arabidopsis thaliana*, and these T-DNA mutant lines were analyzed. The point-mutated recombinant CWPO-C was also generated to determine the oxidation sites of CWPO-C.

2007-P06

ポプラ分化中木部における 4–coumarate:CoA ligase 免疫局在

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Immunolocalization of 4CL in differentiating xylem of poplar

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Abstract: Anti-4-coumarate:CoA ligase (4CL) antiserum were raised using artificially synthesized peptides. They were injected several times into mouse, and then the mouse anti-4CL serum was obtained. Specificity of the anti-serum was confirmed by western blotting and immunoprecipitation techniques. Immunolocalization of 4CL was observed in differentiating xylem cells of *Populus sieboldii* X *P. grandidentata*.

2007-P07

Stereochemistry on the formation of syringylglycerol-8-*O*-4'-(sinapyl alcohol) ether from sinapyl alcohol with enzyme preparations of *Eucommia ulmoides*

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Abstracts: Incubation of a soluble enzyme preparation with [8-^{14}C]sinapyl alcohol (SA) in the presence of H_2O_2 gave [^{14}C]syringylglycerol-8-*O*-4'-(sinapyl alcohol) ether (SGSE). The *erythro* isomer was more favored than the *threo* isomer with 63.2 percentage of diastereomeric excess (% d.e.) at 30min and 26.7% d.e. at 60min, respectively. The *erythro* and *threo* isomers at 60min were levorotatory with 47.4% and 21.6% enantiomeric excess (% e.e.), respectively. Incubation of an insoluble enzyme preparation with [8-^{14}C]SA also gave [^{14}C]SGSE. The *erythro* isomer was more favored than *threo* isomer with 60.8% d.e. at 2min and 11.4% d.e. at 60min, respectively. At 60min (+)-*erythro* and (-)-*threo* isomers were formed with 24.8 and 14.6 enantiomeric excess (% e.e.), respectively. Interestingly, the soluble preparation catalyzed the formation of (-)-*erythro* SGSE, whereas the insoluble preparation did (+)-*erythro* SGSE.

2007-P08

カテキン類の熱変性に対する計算化学解析

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Computor chemistry analysis of thermal transformation of carechins

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Abstract: (+)-Catechin transforms to (+)-epicatechin at high temperature, and they reach to thermodynamically equilibrium state expressible with the equilibrium constant, K. This report deals with the equilibrium constants calculated by several methods of computer chemistry, K_{Calc}, and the comparison of them to experimental value, K_{Expt}. The K_{Calc} by a molecular orbital calculation (RB3LYP/6-31G*) designated qualitatively agreement with K_{Exp}. Which denotes superior of (+)-catechin to (+)-epicatechin and decreases with temperature. However, K_{Calc} quantitatively disagrees with K_{Expt}.

2007-P09

高圧水蒸気蒸留による桐材成分の抽出

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Extraction of constituents from paulownia wood by high-pressure steam distillation

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Abstract: Paulownia (*Pauloumia tomentosa*) wood contains sesamin and paulownin which have a repellent action against insects. In this study, steam distillation of paulownia wood was conducted at two different pressures (1.5 and 2.1MPa) and the distilled oil was analyzed by GC-MS. During high-pressure steaming for paulownia wood, sesamin and paulownin were epimerized. The combined yield based on the dry wood weight under 2.1MPa of sesamin and episesamin was 0.098%, and that of paulownin and epipaulownin was 0.82%. Meanwhile, those of total extraction with alcohol-benzene refluxed for 24 hr were 0.49% and 1.1%, respectively.

2007-P10

白色腐朽菌 *Phanerochaete crassa* WD1694 由来のグリオキサールオキシダーゼの生産と精製

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Production and purification of glyoxal oxidase from a white-rot fungus *Phanerochaete crassa* WD1694

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Abstract: As a preliminary step to analyze localization mechanism of peroxidase reaction at hyphal tips of *P. crassa* WD1694, production and purification of glyoxal oxidase from *P. crassa* WD1694 was studied. The maximum activity of glyoxal oxidase was produced in cultures containing 100 mg/l $MnSO_4$ and 0.05% Tween 80 on day 4 of growth. The harvested culture was filtrated, concentrated, and further purified with DEAE-Sepharose. The purified GLOX was detected as a single band by the analysis of SDS-PAGE.

2007-P11

フラクトメータを用いた腐朽測定値とリグニン分解過程の相互関係

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Relationship between compression strength of decayed wood measured by Fractometer and lignin degradation process

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Abstract: To obtain basic knowledge for detecting the degree of wood decay using Fractometer, relationship between compression strength of decayed wood measured by Fractometer and lignin degradation process was investigated. Sapwood cores of *Cryptomeria japonica*, *Prunus jamasakura*, and *Magnolia obovata* were decayed for 60 days by a brown-rot fungus (*Coriolellus palustri*, FFPRI 0507), a white-rot fungus (*Coriolus versicolor*, FFPRI 1030), and a soft-rot fungus (*Chaetomium globosum*, NBRC 6347). When *C. japonica* and *P jamasakura* cores were decayed, compression strength of each core was decreased. These results suggest that degree of decay in wood can be evaluated using compression strength

measured by Fractometer.

2007-P12

Sphingomonas paucimobilis SYK-6 株の β-アリールエーテル代謝に関与する 4 種の脱水素酵素の機能と立体選択性

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Stereoselectivity and roles of four distinct guaiacylglycerol-b-guaiacyl ether dehydrogenases from *Sphingomonas paucimobilis* SYK-6

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Abstract: Degradation of arylglycerol-β-aryl ether is the most important process of bacterial lignin catabolism. *S. paucimobilis* SYK-6 oxidizes guaiacylglycerol-β-guaiacyl ether (GGE) to α-(2-methoxyphenoxy)- β-hydroxypropiovanillone (MPHPV), and then the ether linkage of MPHPV is cleaved to generate α-glutathionyl-β-hydroxypropiovanillone and guaiacol. We have characterized enantioselective glutathione S-transferases, which are involved in the ether cleavage of different enantiomers of MPHPV. In this study, we found that three GGE dehydrogenases of SYK-6 are involved in the transformation of GGE into MPHPV. LigD1 is essential for the transformation of
(α*R*, β*S*)-GGE and (α*R*,β*R*)-GGE. Both LigD2 and LigD4 participate in the conversion of
(α*S*,β*R*)-GGE and (α*S*,β*S*)-GGE.

2007-P13

Sphingomonas paucimobilis SYK-6 株のプロトカテク酸ジオキシゲナーゼが関与する 3-*O*-メチルガリック酸解裂経路

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Degradation of 3-*O*-methylgallate in *Sphingomonas paucimobilis* SYK-6 by pathways involving protocatechuate 4,5-dioxygenase

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Abstract: *Sphingomonas paucbnobilis* SYK-6 converts vanillate and syringate to protocatechuate (PCA) and 3-*O*-methylgallate (3MGA), respectively. 3MGA is metabolized via multiple pathways involving 3MGA 3,4-dioxygenase, PCA 4,5-dioxygenase (LigAB), and gallate dioxygenase. In this study, we investigated the role of LigAB in syringate metabolism. The reaction product of 3MGA catalyzed by His-tagged LigAB was identified as 4-caboxy-2-hydroxy-6- methoxy-6-oxohexa-2,4- dienoate (CHMOD) and 2-pyrone-4,6-dicarboxylate (PDC), indicating that 3MGA is transformed to CHMOD and PDC by the reaction catalyzed by LigAB. Mutant analysis revealed hat die 3MGA catabolic pathways involving LigAB are functional in SYK-6.

2007-P14

リグニン下流代謝系プロトカテク酸 4，5-解裂経路遺伝子群の転写制御機横

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Transcriptional regulation of the genes involved in the protocatechuate 4,5-cleavage pathway

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Abstract: The protocatechuate (PCA) 4,5-cleavage pathway is the essential metabolic route for lignin catabolism in *Sphingomonas paucimobilis* SYK-6. Here we examined the operon structure of the PCA 4,5-cleavage pathway genes and investigated the transcriptional regulation of the genes.
Reverse transcription-PCR analysis indicated that the PCA 4,5-cleavage pathway genes of SYK-6 consist of three transcriptional units, including the *ligK*-*orf1*-*ligI*-*lsdA* operon, the *ligJ*-*ligA*-*ligB*-*ligC* operon, and the monocistronic *ligR*. Transcription of *ligK* and *ligJ* operons are directly up-regulated by LigR, and this transcriptional activation requires PCA as an inducer.

2007-P15

リグニンモデル化合物の電気化学的酸化（2）、－ 1-phenylethanol 誘導体の酸化反応－

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Electrooxidation of lignin model compounds (2) - Oxidation of 1-phenylethanol derivatives -.

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Abstract: The anodic oxidation of 1-phenylethanol derivatives, 1-(4'-ethoxy-3'methoxyphenyl) ethanol (1G), 1-(4'-ethoxy-3', 5'-dimethoxyphenyl) ethanol (1S) and 1-(4'-ethoxyphenyl) ethano1 (1 P) were investigated for the application to the pretreatment of kraft pulping. The oxidation with 2,6-lutidine, gave the corresponding a-carbonyl derivatives (4-O-ethylacetovanilone : 2G, 4-O-ethylacetosyringone : 2S, 4-ethoxyacetophenone : 2P) in 40-70%. The electrooxidation mechanism of 1-phnylethanols is also proposed.

2007-P16

非木質試料におけるリグニン定量値の評価

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Evaluation of lignin content in non-wood plants

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Abstract: To evaluate the lignin content in non-wood cell walls, leaves and grass stems of various vascular plants were subjected to different kind of wet chemical analyses and these results were compared with the apparent lignin content obtained by Klason procedure. As a method of wet chemical analysis, nitrobenzene oxidation and ozonation were applied. Infrared spectroscopy was also used to estimate the amount of aromatic structures. The comparison of apparent lignin content and the yields of specific degradation products obtained by wet chemical methods suggested that the Klason procedure cannot give the correct lignin content in the case of non-wood cell walls. The amount of aromatic structures estimated by FT-IR was correlated very well with the yield of nitrobenzene oxidation products, which strongly supported the idea that lignin content in non-wood cell walls can be more reasonably expressed by the yields of these specific degradation products rather than Klason procedure.

2007-P17

リグニンの熱分解による機能性炭素への物質変換

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Conversion of lignin to functional carbon materials by pyrolysis

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Abstract: It is attempted that nano-structured and porous carbon materials were synthesized by pyrolysis of lignin. Under anaerobic conditions of a slow heating rate, lignin (alkaline) was converted to a porous carbonaceous material showing 738 m^2/g of BET surface area. Under the same heating conditions, a freeze-dried reverse micelle of lignin converted to a high porous carbonaceous material showing 1003 m^2/g of surface area.

2007-P18

β-5 型リグニンモデル化合物の熱分解− メチル化

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Tetramethylammonium hydroxide (TMAH) thermochemolysis of lignin: Behavior of β–5-type lignin model compounds

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Abstract: Phenolic 2-arylcoumarans **1-6** were subjected to tetramethylammonium hydroxide (TMAH) thermochemolysis (500 ºC/4 s) to investigate reactions occurring in lignin specifically under these conditions. Products were monitored by gas chromatography/mass spectrometry (GC/MS). GC/MS signals corresponding to dimers overwhelmed all GC/MS traces. (2-Phenyl-2,3-don-3-yl) methan-1-ols (**1** and **6**) predominantly gave 2,3,3',4'-tetramethoxystilbenes involving in a loss of the γ-CH_2OH substituent. 3-Methyl-2-phenyl-2,3-dihydrobenzofurans (**2**-**5**) gave a mixture of 1-(3,4-dimethoxyphenyl)-2-(2,3-dimethoxyphenyl)-1-methoxypropans and 2,3,3’,4’- tetramethoxy-stilbenes having the γ-methyl group. Side chains –$CH=CHCH_2OH$ and -COOH on ring B were simply methylated to produce the corresponding methyl ether and ester, respectively. A –$CH=CHCH_3$ Side chain was preserved intact, whereas a –CH=CHCHO side chain changed to a -CHO side chain. This was confirmed by isolating 5-formyl-2,3,3',4'-tetramethoxystilbene as an off-line TMAH thermo- chemolysis product from 3-[2-(4-hydroxy-3-methoxyphenyl)-3- hydroxymethyl-7-methoxy-2, 3- dihydrobenzofuran-5-yl] propenal.

2007-P19

DSC で検出されるリグニンのガラス転移温度に対する加熱前処理の影響ー 針英樹と広葉樹の違いおよびメトキシ基量の影響

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Effects of DSC pre-heat treatment on the glass-transition temperature of lignin -Difference between softwood and hardwood lignin, and effect of methoxy contents

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Abstract: In the DSC analysis of lignin, thermal treatment "pre-heat treatment" is usually required to remove thermal history before measurement. However, glass transition temperature of softwood kraft lignin was significantly affected by this pre-heat treatment. By contrast, such Tg increase was not observed for hardwood kraft lignin. Typical structural difference between softwood and hardwood lignin can be found in the aromatic ring structure. Therefore, DSC analysis was also performed for various lignins which have different S/G. However, clear correlation could not be detected between S/G and Tg increases. S/G would be not solo factor to such Tg increase of lignin.

2007-P20

リグニンを基盤とした新規ポリマーの創製

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Development of novel polymer based on lignin

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Abstract: In Japan, lignosulfonate is mainly used for water reducing agent of cement and dye dispersant. In order to expand in application, we tried to produce a novel polymer based on the lignosulfonate. We obtained ion-conducting polymers from sodium lignosulfonate by substitution of sodium ion to imidazole compound. The

polymers showed higher conductivity with longer the side chain of imidazole compound. Purification of sodium lignosulfonate led low ion conductivity. It is suggested that impurity contained in the sodium lignosulfonate, such as sugars, induced the ion conductivity.

2007-P21

イオン性相互作用によるリグノスルホン酸の生体関連物質吸着能

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Functionalization of lignosulfonic acid: Its adsorption property to catch bio-related substances by ionic interactions

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Abstract: Poly-ion complexes of anionic lignosulfonic acid (LSA) with cationic poly(L-lysine) (PLL) were prepared by spontaneous precipitation from mixed aqueous solutions adjusted at different pHs. Fourier transform infrared (FTIR) measurements and elementary analysis for the complexes revealed the presence of strong ionic interactions between the sulfonic anion of LSA and the □-aminocation of PLL. Circular dichroism measurements revealed that an α-helix conformation of PLL changed to a random coil conformation when the complexes were formed. An adsorption property of LSA to catch nicotine compounds was also examined by FTIR measurements and high performance liquid chromatography.

2007-P22

高圧水蒸気蒸留による竹からのチロシンの効率的な抽出

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Development of the efficient extraction of tyrosine from grown bamboo shoot by high-pressure steam distillation

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Abstract: It was confirmed that large quantities of tyrosine is contained in grown bamboo shoot by solid state CPMAS ^{13}C-NMR analysis. Because of its chemical structure, tyrosine is not distillable with common steam distillation method. Therefore, a new high-pressure steam distillation method was evaluated for efficient extraction of tyrosine from bamboo shoot. From the distilled essential oil of madake bamboo shoot, 4-hydroxy styrene and 3-methoxy-4-styrene derivatives were isolated and identified.

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2008-101

イネのケイヒ酸モノリグノール経路遺伝子の検索と遺伝子発現解析

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Computational identification and expression analysis of monolignol biosynthesis pathway genes in rice

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Abstract: It is still unknown which gene set works in monolignol biosynthesis in rice. Here, we surveyed computationally the genes encoding enzymes of the cinnamate/monolignol pathway in all rice protein sequences. Expression analysis of the rice genes showed diversification of the qualitative and quantitative expression patterns among the gene family members. The most part of the genes were classified into 5 groups with the organ-specific expression pattern using Self Organizing Maps method. The fact that all the groups have plural enzyme genes of the monolignol biosynthesis pathway implies role and responsibility of the gene sets for monolignol synthesis in each organ.

2008-102

TDNA 挿入変異体を用いたシロイヌナズナ 4CL 遺伝子の機能解析

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The functional analysis of 4-coumarate:CoA ligase genes in *Arabidopsis thaliana* by using T-DNA tagged mutants

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Abstract: 4-Coumarate:CoA ligase is one of key enzymes in biosynthesis of monolignols in many plants. *Arabidopsis thaliana* has five 4CL genes (*At4CL1-At4CL5*) in its genome. To understand the function of the genes for 4CL in the lignin biosynthesis, the phenotypes of two T-DNA inserted mutants (*At4cl1*/*At4cl1* and *At4cl2*/*At4cl2*) were analyzed in this study. We have measured 4CL activity of the mutants with crude enzymes from their stems. The activities of *At4cl1*/*At4cl1* and *At4cl2*/*At4cl2* lines were 12.5% and 43.7% of that in control line, respectively. As the results of lignin specific staining, decrease in lignin content and composition of syringyl residue in *At4cl1*/*At4cl1* line were revealed, whereas those in *At4cl2*/*At4cl2* line were nearly identical to the control plant. The mutant and control lines showed similar development pattern except for a *At4cl1*/*At4cl1* line, SALK142526, which exhibited dwarf phenotype. These results suggest that *At4CL1* plays crucial roles in lignin biosynthesis in *A. thaliana*.

2008-103

改変型植物酸性 peroxidase の酵母での発現と精製（2）

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Heterogeneous expression and purification of modified plant peroxidase (2)

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Abstract: Lignin peroxidase of *Phanerochaete chrysosporium* can oxidize the environmental pollutants and lignin by assuming Trp-171 near the surface of the protein to be a catalyst site. CWPO-C that is a kind of poplar peroxidases can oxidize sinapyl alcohol, and is presumed that Tyr-74 arid Tyr-177 exposed to the surface of the protein are the catalyst sites. We introduced the mutations into *prxA3a*, a POX gene of *Populus kitakamiensis*, changed the amino acid residues at the corresponding positions to Trp and Tyr residues, and examined the changes in the substrate specificities.

2008-104

選択的リグニン分解菌が産生する菌体外脂質関連代謝物の構造解析

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Structural analyses of extracellular lipid-related metabolites produced by a selective lignin degrading fungus

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Abstract: Wood-rot fungus, *Ceriporiopsis subvermispora* can degrade lignin without intensive damage of cellulose. We have been focusing on extracellular metabolites participating in the selective ligninolysis, and characterized a series of unique metabolites, ceriporic acids. Important function of ceriporic acid is inhibition of cellulose degradation by hydroxyl radicals (HO・) produced by the Fenton reaction system. Here, we investigate extracellular lipid-related metabolites using liquid chromatography, mass spectrometry and nuclear magnetic resonance spectrometry. New metabolites including a series of ceriporic acids were found and analyzed.

2008-105

抗炎症剤であるジクロフェナクおよびメフェナム酸の白色腐朽菌による毒性除去

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Removal of toxicities of anti-inflammatory drugs, diclofenac and mefenamic acid, by white rot fungus *Phanerochaete sordida* YK-624

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Abstract: At present, there is an increasing concern on the presence of pharmaceutical compounds in the environment mainly due to their potential risk to the aquatic environment. In this study, diclofenac (Dic) and mefenamic acid (Mef), which are used widely as non-steroidal anti- inflammatory drugs and are ubiquitously found in the water sample, were treated with white rot fungus *Phanerochaete sordida* YK-624 under ligninolytic condition with low-nitrogen and high- carbon culture medium. After 6 days of fungal treatment, Dic completely disappeared and Met decreased by about 90%. During the treatment of Dic, two major metabolites, 4'-hydroxydiclofenac and 5-hydroxydiclofenac, were found in the cultures. On the other hand, a major metabolite of Mef was 3'-hydroxymefenamic acid. Toxicities of Dic and Mef before and after fungal treatment were evaluated by acute lethal toxicity test using freshwater crustacean *Thamnocephalus platyurus*. The profiles for removal of toxicities of Dic and Mef and decrease in concentrations of both drugs during treatment were very similar. These results suggested that hydroxylation of Dic and Mef is mainly involved in detoxification of these drugs.

2008-106

冬虫夏草（*Cordyceps*）菌による多環式芳香族炭化水素および塩素化ダイオキシン分解の試み

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Attempts to degrade polycyclic aromatic hydrocarbons (PAHS) and chlorinated dioxins by *Cordyceps* species

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Abstract: Degradation experiments of chlorinated dioxins using *Cordyceps* species were carried out. As chlorinated dioxins, 2,7-dichloro-, 2,3,7-trichloro, 1,3,6,8-, 1,3,7,8-, and 1,3,7,9-tetrachloro- dibenzo-p-dioxin and 2,4,8-trichhrodibenzofuran were used. *Cordyceps brongniartii* and *Cordyceps militaris,* were selected based on the ability of 2,7-dichlorodibenzo-p-dioxin (2,7-diCDD) degradation. 2,7-DCDD, 2,3,7-triCDD and 2,4,8-triCDF were biotransformed to hydroxyl compounds by *C.militaris*. PAHs were degraded rapidly in medium containing chitin or chitosan by *C. militaris* and *C. brongniartii*. Phenanrhrene and pyrene were completely disappeared in these medium. In addition, benzo [a] pyrene and indeno [1,2,3-c,d] pyrene also were degraded extensively.

2008-107

Biodegradation of phenanthrene, an aromatic hydrocarbon by *Polyporus* sp. S133 in liquid medium

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Abstract: The effect of adding several concentrations of tween 80 and agitation rate to increase degradation rate of phenanthrene by using *Polyporus* sp. S133 collected from contaminated soil was studied. A maximal degradation rate (92%) was obtained when *Polyporus* sp. S133 was cultured under agitation of 120 rpm for 30 days, as compared to just 44% degradation in non-agitated cultures. The degradation rate increased as the amount of tween 80 added increased. The rate in agitated cultures was about 2 times that in non-agitated cultures. The mechanism for degradation of phenanthrene with the fungus through identification of the metabolites was found.

2008-108

微生物機能を用いた植物バイオマス資源（リグニン）の新規ポリマー原料への変換技術と新しい機能性材料の製造 III

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Studies of technology that converts plant biomass (lignin) into new polymer materials using bacterial function and products novel functionality materials, III

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Abstract: *Sphingomonas paucimobilis* SYK-6 is able to grow on various lignin-derived biaryls, and 2-pyrone-4,6-dicarboxylic acid (PDC), an intermediate of these compounds, can be used as the polymer materials. In a previous study, we built a bioreactor to produce PDC with genetic technique, and succeeded in producing PDC from protocatechuate, vanillin, vanillate, and *p*-hydroxybenzoate. In this study, we examined the feasibility of industrial PDC production by using lignosulfonic acid, one of the actual lignin resolvent. The existence of resolvent of lignosulfonic acid did not inhibit PDC production from 5 g/L vanillin. This result raise the possibility of industrial PDC production built into the paper-forming process.

2008-109

単離リグニンの両親媒性化とその機能評価

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Conversion of lignin to amphiphilic compounds and their characterization

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Abstract: The acetic acid lignin (AL) was converted to an amphiphilic polymer by derivatization of AL with several polyethylene glycol diglycidylethers (PEGDE) to make use of them as a nonionic surfactant. The derivatives revealed significant surface activity, such as reduction of water surface tension and critical micelle concentrations (CMC), although both PEGDE and PEG showed very weak. The surface activity of AL derivative was improved by the reaction with monoepoxide compound, ethoxy-(2-hydroxy)-propoxy-polyethylene glycol glycidylether (PEGGE). The hydrophile-lipophile balance

(HLB) suggested these derivatives were suitable to use as emulsifiers and detergents. In addition, these derivatives were found to have higher biodegradability than lignin. Consequently, these derivatives are promising as environmentally-friendly surfactants.

2008-110

バイオエタノール生産副産物加水分解リグニンを原料とするポリウレタンの調製と物性

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Preparation and properties of polyurethane derived from hydrolysis lignin obtained as byproduct of bioethanol

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Abstract: Polyurethane (PU) foams were prepared using hydrolysis lignin (HL) obtained as a by-product of bioethanol industry. Four kinds of HL's from Russia and New Zealand were utilized. Sodium lignosulfonate (LS) obtained as a by-product of the pulping industry was also used as a reference. HL and LS polyols were obtained by dissolving HL and LS in diethyleneglycol (DEG) and polyethyleneglycol (PEG200). In this study, PU foams were obtained by reacting the above polyols with poly(phenylene methylene) polyisocyanate (MDI) using a small amount of water as foaming reagent. Apparent density of PU foams was in a range from 0.04 to 0.08 g/cm^3. Compression strength (δ10) was in a range from 0.1 to 0.4MPa. Thermal degradation was ca. 300 ºC and mass residue at 500 ºC was ca. 35 %. Glass transition temperature (Tg) of PU foams from DEG was ca. 100 ºC regardless of kinds of lignin. In contrast, Tg of PU foams from PEG was ca. 50 ºC. Thermal conductivity was ca. 0.03 W/mK which indicates that PU foams show excellent insulation effect. It is concluded that PU foams derived from HL can be applicable for housing materials as an insulator.

2008-111

リグニンスルホン酸塩、エチレングリコール及びグリセリンを原料とするエポキシ樹脂の合成と熱的性質

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Synthesis and thermal properties of epoxy resins from ligninsulfonate, ethylene glyco1 and glycerol

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Abstract: Sodium ligninsulfonate (LS) was dissolved in glycerol (GLY) and the obtained mixture was allowed to react with succinic anhydride to form a mixture of ester-carboxylic acid derivatives (LS-GLY polyacid, LSGLYPA). LS-ethylene glycol (EG)-polyacid (LSEGPA) was also prepared from EG. The mixture of LSGLYPA and LSEGPA was reacted with glycerol diglycidyl ether (GLYDGE) in the presence of catalytic amount of dimethylbenzy1amine to form epoxy resins. The molar ratio of epoxy groups to carboxylic acid groups ([EPOXY]/[AA] ratio, mol/mol) was maintained at 1.1. The contents of LSGLYPA in the mixture of LSGLYPA and LSEGPA (LSEGPA content) were varied from 0 to 100 %. Thermal properties of epoxy resins were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG). Glass transition temperatures (Tg's) of epoxy resins increased with increasing LSGLYPA contents suggesting that glycerol act as a cross-linking forming agent in epoxy resin networks. Thermal decomposition temperatures (Td's) of epoxy resins were almost constant regardless of LSGLYPA contents.

2008-特別講演

有機合成化学的アプローチによる木質バイオマス成分研究 ー木材の総合研究と総合利用ー

中坪文明
京都大学大学院農学研究科

Studies on the woody biomass constituents by organic synthetic approach -Toward total utilization of woody biomass by interdisciplinary research-

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Abstract: Studies on the woody biomass constituents by organic synthetic approach toward total utilization of woody biomass by interdisciplinary research are reported: general synthetic method for oligo- and polylignols and novel selective cleavage method for β-O-4 in the lignin chemistry; chemical synthesis of cellulose and its extended research to the preparation and characterization of Langmuir-Blogett films, cellulosic photocurrent generation thin films in the cellulose chemistry, and syntheses of hydrolysable and condensed tannins and their properties in tannin chemistry.

2008-201

クラフトーアントラキノン蒸解におけるアントラキノン浸透処理の効果

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Effects of anthraquinone compounds impregnation in kraft cooking

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Abstract: In order to increase the pulp yield by anthraquinone compounds, it is very important to impregnate anthraquinone compounds efficiently into wood chips. In this report, the effect of impregnation treatment before kraft cooking process was investigated using the laboratory cooking equipments. By measuring 9,10-anthraquinone in the liquor after the impregnation treatment, the impregnation conditions (temperature, time, active alkali charge, and liquor/wood ratio) were optimized. By the employment of the optimized impregnation condition, the pulp yield was improved by about 0.4% when compared at kappa 16.

2008-202

Analysis of lignin by the use of whole wood solution consisting of DMSO-LiCl

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Abstract: The whole lignin in wood was analyzed by the use of whole wood solution consisting DMSO/LiCl. The wood solution formed gel after standing one day at room temperature. Concentration of milled wood required for gel formation was dependent on the milling time. The gram absorptivity of lignin at 280nm was obtained by the use of this whole wood solution. The ^{1}H-NMR spectrum of whole wood solution clearly shows the lignin aromatic part without any interfering overlapping peak. This is the first time to obtain information of aromatic part in whole lignin directly without any kind of isolation treatment.

2008-203

イオン液体処理過程における木材成分の溶出挙動とリグニンの変化

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Structural change of lignin during a process of wood components dissolution into ionic liquid

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Abstract: Wood meals of *Abies sachalinensis* and three eucalyptus were treated with one of the ionic liquids: 1-n-buthyl-3-methylimidazolium chloride ([bmim]Cl). The contents of lignin and carbohydrates in the insoluble fractions were determined. The insoluble fractions were applied to analytical pyrolysis for lignin characterization. The results showed that cellulose dissolved significantly during the [bmim]Cl treatment. The pyrograms of insoluble fraction were quite similar to that of untreated wood. Moreover, the amount of β–O-4 linkage in lignin were slightly decreased by this treatment. Therefore, it showed that chemical characteristics of lignin were hardly changed by the [bmim]Cl treatment.

2008-204

イオン液休中での β–O-4 型リグニンモデル化合物の反応性

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Reactivity of β-O-4 type ligmin model compounds in ionic liquids

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Abstract: Structural stabilities and reactivity of lignin in ionic liquids (ILs) have been examined using lignin model conpounds. *Threo* type guaiacylglycerol-β-guaiacyl ether (T-GG) was decomposed similarly to [Z] isomer of enol-ether, [Z]-3-(4-hydroxy-3-methoxyphenyl)-2- (2-methoxyphenoxy)-2-propenol (Z-EE), as *erythro*GG (E-GG), although decomposition rates of E-GG were faster than TLGG. Hardwood type β-O-4 lignin model compounds, threo-guaiacyl- glycerol-β–syringyl ether (T-GS) was decomposed rather faster than softwood type β-O-4 lignin model compounds, and nonphenolic model compounds were relatively stable in ILs. These results could be comparable with the structural stability of β-O-4 type lignin model compounds in alkaline conditions, although the reaction mechanisms in ionic liquids have not been elucidated.

2008-205

イオン液体中での木材の反応挙動 −針葉樹と広葉樹の比較−

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Reaction behavior of wood in an ionic liquid -Comparisons between softwood and hardwood-

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Abstract: Reaction behavior of western red cedar (*Thuja plicata*) and beech (*Fagus crenata*) as treated in an ionic liquid, 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]) which can dissolve cellulose was investigated. Much residue after [C2mim][Cl] treatment can be obtained from western red cedar, compared to beech. Lignin content in the residues from western red cedar is higher than in that from beech. It is also found that the degradation of lignin occurs by the cleavage of the ether linkage with [C2mim] [Cl] treatment.

2008-206

β-エーテル型リグニン 2 主体モデル化合物の熱分解における同位体効果

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Kinetic isotope effects in pyrolysis of lignin β-ether model dimers

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Abstract: From the comparison of the reactivities and the pyrolysis products of lignin β-ether- type dimers between an open-top and a closed ampoule reactors, We have proposed some radical chain reactions starting from the H-Abstraction reactions. In this paper, kinetic isotope effects observed in the deuterated dimers are described. Based on the results, possibilities of radical chain reactions in lignin pyrolysis are discussed.

2008-207

木材ガス化におけるセルロースーリグニン間の相互作用

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Interactions between cellulose- and lignin-derived pyrolysis products in gasification

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Abstract: Interactions between cellulose- and lignin-derived pyrolysis products were studied under gasification conditions (N_2/600ºC/40-80s). A dual-space closed ampoule reactor was used to eliminate the solid-phase interactions, and careful comparison of the resulting data with those of the pyrolysis of the mixed samples gave some insights into the solid - and vapor-phase interactions separately. As a result, significant interactions were observed which include acceleration of the gasification of cellulose-derived volatiles and the formation of methane and catechols from lignin. These influences are explained with a proposed mechanism, in which the cellulose-derived volatiles act as H-donors while the lignin-derived volatiles (radicals) as H-acceptors.

2008-208

^{13}C 標識テトラメチルアンモニウムヒドロキシドを用いた熱分解−メチル化法によるリグニン中の β-O-4 型構造およびシンナミルアルコール末端基の検討

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Chamcterization of β–O-4 and cinnamyl alcohol end units in lignin by ^{13}C-labeled TMAH thermochemolysis

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Abstract: To estimate the origins of pyrolysis-methylation products from lignin, ^{13}C-labeled tetramethylammonium hydroxide (^{13}C-TMAH) thermochemolysis was applied to lignins pre-methylated with diazomethane. Products were monitored by gas chromatography/mass spectrometry. The number of ^{13}C atom incorporated in the products showed that in guaiacyl synthetic lignin (DHP) coniferyl alcohol end units are present in a 7/3 of 4-O-/γ-O-etherified forms, while in Japanese cedar wood they are present in roughly 6/4 ratio. In both lignins, guaiacylglycerol moieties involving in β-O-4 linkage provided the same amount of 1-(3,4-dimethoxyphenyl)-1,2,3- trimethoxypropane consisting of two isomers (*erythro*- and *threo*-forms) from end units and core units. Although G-DHP provided many dimer products, the cedar provided those in a trace amount.

2008-209

リグニンモデル化合物の間接電解酸化反応

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Indirect electrooxidation of lignin model compounds

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Abstract: Indirect electrooxidation of lignin model compounds using N-hydroxyphthalimide (NHPI) as an mediator was studied to introduce carbonyl group at α-position. Monomeric lignin models, 1-(4'-ethoxy-3'-methoxyphenyl)ethanol (1G), 1-(4'-ethoxy-3',5'-dimethoxyphenyl)ethanol (1S) were oxidized to the corresponding carbonyl compounds (2G, 2S) in high yields (over 90%) and high current efficiencies (ca. 90%). In the indirect electrooxidation of dimeric lignin model (4-ethoxy-3-methoxyphenylglycerol-β-guaiacylether (3)), α-carbonyl dimer (3-hydroxy-1-(4-ethoxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-propan-1-one (4)) was formed, while 4-O-ethylvanillin was formed in the direct oxidation. These results suggest that NHPI-mediated indirect electrooxidation is an effective method for α-carbonyl introduction to natural lignin structures.

2008-210

モノリグノール配糖体によるシリンギル型 DHP の生成挙動の解析（II）−pH の影響−

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Mechanistic study of the dehydrogenative polymerization using γ-glycosylated monolignols, II
-The effect of pH on the formation of syringyl dehydrogenation polymers

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Abstract: Horseradish peroxidase (HRP)-catalyzed polymerization of syringyl-type monolignol glycoside (iso-S) was carried out in homogeneous aqueous media of different acidity and was monitored by UV spectroscopic and GPC techniques, in order to determine the effect of pH on the formation of syringyl dehydrogenation polymers (S-DHPs). It was found that at lower pH, the S-type quinone methide intermediates

(S-QM) were quenched more rapidly to result in more efficient formation of S-DHP. The results for the polymerization of S-alc also support this view. Structural analyses on the S-DHPs demonstrated that the reaction of S-QM with water was promoted at low pH, indicating its higher reactivity than that in neutral media.

2008-211

TOF-SIMS によるリグニン S／G 比顕微分析法の開発

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The syringyl/guaiacyl (S/G) ratio of lignin estimated by TOF-SIMS

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Abstract: The syringyl/guaiacyl (S/G) ratios were estimated by time-of-fright secondary ion mass spectrometry (TOF-SIMS) using lignin model compounds and the transverse section of the xylem of *Acer micranthum*. The result showed that the value of S/G ratios detected by TOF-SIMS and the molar S/G ratios were similar in the spectra of 8-O-4' polymers. In other hands, the S/G ratios calculated in the spectra of monomer and dimer model compounds were much higher than the molar S/G ratios. This result suggests that the estimation of S/G ratio by TOF-SIMS is reliable in lignin polymers. Further experiments were needed to estimate the reliability of S/G ratio calculated in TOF-SIMS spectra.

2008-212

リグニン中の枝分かれ構造の探索 - 非フェノール性ダイベンゾダイオキソシン構造の ^{1}H−および ^{13}CNMR 化学シフトの特徴 -

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Characteristics in ^{1}H- and ^{13}C-NMR chemical shifts of non-phenolic dibenzodioxocin model compounds as branch-points in lignin

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Abstract: Non-phenolic dibenzodioxocin compounds modelling the 4-O-β-ethers that would be generated following radical coupling with a monolignol were synthesized to explore branch-points in lignin. NMR measurements on acetylated models revealed that the aromatic carbons (C1) attached to the side chain of a dibenzodioxocin had significantly different chemical shifts between phenolic and non-phenolic models (□δ~3.6 ppm) while the other side chain proton and carbon shifts (α- and β-positions) were similar. It is suggested that phenolic and non-phenolic dibenzodioxocin models can be distinguished from each other by NMR, particularly via long-range correlation (HMBC) NMR experiments.

2008-213

オイルパーム材のバイオエタノール製造原料としての特性

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The characterization of oil palm trunk as a material of bio-ethanol production

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Abstract: Using some samples cut out vertically and radially from 25 years old *Elaeis guineensis* (oil palm) trunks, chemical composition was determined. As a result, as higher and innerer the oil palm trunk, the more hot water extractable glucose were observed. The hot water extractable glucose, fructose and sucrose

contents of oil palm trunk were roughly estimated as 63, 13 and 11 kg, respectively. Estimated ethanol production per cultivated area was 7.4 kL/ha. The ethanol yields of fermentation of sugar liquors from oil palm wood meals by *Zymomonas mobilis* were almost same as that from glucose solution, so it would appear that there was no fermentation inhibitor in oil palm wood meal.

2008-214

高圧下におけるツヤ酸の水蒸気蒸留とその化学転換

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Result of the steam distillation and the chemical changes of thujic acid under high-pressure

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Abstract: Thujic acid, knows as antibacterial substance, is a component of the essential oil extracted from Western Red Ceder (*Thuja plicata*). Since the structure of thujic acid is unstable, it is expected to undergo chemical transformation easily. Therefore, the chemical transformations of thujic acid under high-pressure steam condition and under UV radiation were observed. By high- pressure steam treatment, thujic acid was transformed into cumin acid and m-cumin acid under acidic condition, while novel compound was produced under basic condition. Furthermore, thujic acid transformed into novel compounds by UV radiation.

2008-215

樹皮の酵素糖化における新規前処理技術の開発

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Development of novel pretreatment for enzymatic saccharification of bark

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Abstract: In this study, saccharification of bark by enzyme hydrolysis was investigated. To enhance the enzyme accessibility to the polysaccharides in the cell wall, such as cellulose and holocellulose, hydrothermal pretreatment with carbon dioxide was conducted. The results of the enzyme hydrolysis showed that the monosaccharide yield using pretreated bark reached 36%, whereas that using non-pretreatment sample was about 10%. More than 95% of the generated monosaccharide was glucose. This results suggested that the secondary wall which main component is cellulose hydrolyzed effectively by enzyme. The yield of glucose on the basis of a-cellulose reaches about 80%.

2008-216

ユーカリ樹皮のリグニン分布と酵素糖化性

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Lignin distribution influences enzyme succharification of bark in *Eucalyptus*

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Abstract: Inner bark of *Eucalyptus* is composed of sieve tube member, companion cell, phloem parenchyma cell, phloem ray parenchyma cell and phloem fiber. Phloem fiber has a thick secondary wall in which syringyl lignin is accumulated. After the inner bark is exposed to the acidified hot water with CO_2 at 200 degree Celsius, Primary wall of parenchyma cell shows highly swollen structure and secondary wall of phloem fiber has many clefts with a several nanometer width. These cell walls are completely degraded by the treatment with enzymes contained cellulase, xylanase, pectinase and amylase.

2008-217

Gmelina arborea と *Swietenia macrophylla* の樹皮から新規フェニルプロパノイド関連成分の単離同定とそれらの抗酸化活性

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Chemical constituents from *Gmelina arborea* and *Swietenia macrophylla* bark and their antioxidant activity

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Abstract: A new phenylethanoid glycoside,(-)-p-hydroxyphenylethyl[5’’’-*O*-(3,4-dimethoxy- cinnamoyl)-β-D-apiofuranosyl(1’’’→6')]- β-D-glucopyranoside, was isolated from *Gmelina arborea* bark together with tyrosol, (+)-balanophonin, gmelinol, 2,6-dimethoxy-*p*-benzoquinone, and 3,4,5- trimethoxyphenol. The 3,4,5-trimethoxyphenol exhibited a moderate antioxidant activity. From *Swietenia macropkylla* bark, a new phenylpropanoid-substituted catechin, namely, swietemacrophyllanin [(2R*,3S*,7"R*)-catechin-8,7"-7,2"-epoxy-(methyl 4",5"-dihydroxyphenyl- propanoate)] was isolated together with catechin and epicatechin. The swietemacrophyllanin had strong antioxidant activity.

2008-P01

担子菌のラッカーゼ遺伝子を導入した組換え植物における雄性不稔の解析

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Analysis of male sterility in transgenic plants with the chimeric gene for fungal laccase

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Abstract: Transgenic tobacco plants with the chimeric gene for fungal laccase exhibited mate sterility without any influence of pollen viability. Frequencies of the male sterility in the plants depended on the laccase activities in their anther tissues. Since lignification in endothecium of the anther tissue is essential for normal dehiscence of the organ to distribute pollen grains, we analyzed lignin characteristics in the tissue. Results from histochemical and wet chemical analyses indicate that lignin contents in the transgenic tissues are unchanged. By contrast, abnormal deposition of flavonoid in epidermis layer of the transgenic anther was revealed by vanillin staining of the anthers. These results suggest that laccase expression does not affect the lignin biosynthesis but does flavonoid deposition in the transgenic anthers.

2008-P02

カバノアナタケ菌 IO･U1 株に感染した 2 種類のシラカンバ幼植物体クローンにおけるフェノール性化合物の沈着とペルオキシダーゼ活性

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Phenolics deposition and peroxidase activity in two types of Japanese birch plantlet clones infected with *Inonotus obliquus* IO-U1 strain

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Abstract: Two types of Japanese birch clone (Tohoku and No.8) plantlets were used in order to investigate the time-course changes of phenolics deposition and peroxidase activity in Japanese birch (*Betula platyphylla* var. *japonica*) plantlets infected with *Inonotus obliquus* which causes a canker-rot disease of birch tree. In intact and wounded plantlets after 12 hrs of treatments, phenolics deposition was not detected in the both clones. On the other hand, in infected both clones, phenolics deposition was observed in the vessels, wood fibers, and parenchyma cells. In the case of Tohoku clone, peroxidase activity was detected near the infection site after 2

hrs of inoculation, in the vessel cells after 4 hrs, and in the sclerenchyma cells after 30 days.

2008-P03

高活性リグニン分解菌 *Phanerochaete sordida* YK−624 株における新規リグニンペルオキシダーゼ高発現株の特性

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Properties of novel lignin peroxidase-high expression transformants from *Phanerochaete sordida* YK-624

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Abstract: In our previous reports, we have cloned YK-LiP1 and YK-LiP2 encoding genes (*ylpB* and *ylpA*, respectively) from *Phanenchaete sondida* YK-624, and constructed homologous expression transformants introducing these genomic DNAs which were regulated by GPD promoter. In the present study, we investigated ligninolytic properties of these transformants, A-11 (*ylpA* transformant) and B-3 (*ylpB* transformant). These transformants A-11 and B-3 showed higher ligninolytic activity than wild type *P. sordida* YK-624. Moreover, high glucose conversion was observed in the enzymatic saccharification of wood meal which was inoculated with A-11 or B-3, compared with wild type *P. sordida* YK-624. These results suggest that high expression of YK-Lip genes improve ligninolytic activity and selectivity of *P. sordida* YK-624.

2008-P04

白色腐朽菌の菌体外ペルオキシダーゼ反応の局在化について

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Localized extracellular peroxidase reaction of a white-rot fungus *Phanerochaete crassa* WD1694

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Abstract: Distribution of extracellular peroxidase reaction of a white-rot fungus *Phanerochaete crassa* WD1694 was visualized by peroxidase activity staining. The results showed that the extracellular peroxidase reaction of *P. crassa* WD1694 occurred only on the fungal bodies and not in the culture fluids. Further studies about the extracellular peroxidase reaction on the fungal bodies of *P. crassa* WD1694 revealed the occurrence of intense peroxidase reaction at the hyphal tips that lacked fungal slime. Manganese peroxidase and glyoxal oxidase were determined as major enzymes that worked in the peroxidase reaction at the hyphal tips. The significance of the extracellular peroxidase reaction at the hyphal tips on the ligninolytic mechanism of white-rot fungi was discussed.

2008-P05

The pretreatment of corn stover by wood-rotting fungi for the production of bio-ethanol

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Abstract: 40 strains of wood-rotting fungi (33 strains of white-rot fungi and 7 strains of brown-rot fungi) were screened for the pretreatment of bio-ethanol production made of corn stover. Cellulase was used for cellulose saccharification from corn stover pretreated by wood-rotting fungi to test the efficiency of pretreatment. As a result, B-2 a strain of brown-rot fungus was selected for corn stover pretreatment. We determine the composition in corn stover pretreated by B-2 fungus. Although the lignin content increased to 28.3% (control: 25.7%), the glucose yield in cellulose saccharification in corn stover pretreated by B-2 was increased by 150%.

2008-P06

糖質結合モジュール（CBM−CFP）融合タンパクを用いた木材酵素糖化前処理物の解析

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Surface analysis of wood biomass pretreated for enzymatic saccharification by carbohydrate binding module

(CBM)-cyan fluorescent protein (CFP) complexes

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Abstract: Carbohydrate binding modules (CBMs) are noncatalytic substrate binding domains of cellulolytic enzymes. Here we used fluorescent labeled recombinant CBMs specific for crystalline cellulose (CBM3) and non-crystalline cellulose (CBM28) to analyze the complex surfaces of wood tissues pretreated by chemical, thermal and physical methods. Linear correlation between enzymatic saccharification yield and the adsorption of the two CBM-CFP complexes was obtained for the chemically delignified wood. Adsorption of the two CBM-CFP complexes to the physically disrupted wood was much lower than that of the chemically delignified wood. Fluorescent microscopy revealed that CBM-CFP complexes adsorbed preferentially on fibrillated wood tissues but direct adsorption of CBM-CFP complexes on the surface of delignified wood fibers were observed. Thus the quantitative fluorometric method clarified the linear dependency of saccharification yield on exposure of cellulose surfaces in delignified wood.

2008-P07

難揮発性化合物の高圧水蒸気蒸留

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High-pressure steam distillation of nonvolatile compounds

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Abstract: It has been reported that High-pressure steam distillation method allowed distillation of high boiling compounds and nonvolatile compounds which are considered difficult to be distilled. With using this method, thujic acid and hinokitiol were successfully distilled from *Thuja plicata* at the condition of 1.6MPa, 200ºC. The aim of this study is to estimate the availability of high-pressure steam distillation method by observing the distillation behavior of model compounds for further application of this method. In this study, curcumin, known as nonvolatile compound, was chosen as model compound. Curcumin was distilled nearly 1000% within 20mins at the condition of 1.6MPa, 200ºC.

2008-P08

オルガノソルブリグニンアルキルエステル／ポリ（e ーカプロラクトン）ブレンドの均一混合スケールの評価

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Evaluation of size of heterogeneity in blends of poly(e-caprolactone) with organosolv lignin alkyl esters

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Abstract: Organosolv lignin (OSL) alkyl esters (carbon number *n*, 2-5) were synthesized by a homogeneous reaction with different acyl anhydrides/4-dimethylamino pyridine in pyridine solution. The miscibility of the esterified OSLs with poly(e-caprolactone) (PCL) has been investigated previously, mainly through the evaluation of the glass transition temperature (*Tg*) using differential scanning calorimetry (DSC). DSC analysis has revealed that the blends of OSL esters with *n* = 3-5 with PCL showed a composition-dependent shift in *Tg*. Therefore, the blend systems can be regarded as miscible ones in a scale of *Tg*-detection, usually assumed to be less than a couple of tens of manometers. To ascertain the state of miscibility of the blends precisely, they were investigated by using dynamic mechanical analysis (DMA) and solid-state ^{13}C CP/MAS NMR. A detailed estimation of the *Tg* by DMA revealed that the blends with *n* = 3-5 shows a single *Tg*, which varies with composition. Taking into account the $\mathrm{T}_{1p}^{\mathrm{H}}$ estimated by solid-state NMR, it was suggested that the miscible combinations mix on a scale between ca. 5 and 15 nm.

2008-P09

リグニンの表面特性に関する研究

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Study on surface properties of lignins

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Abstract: Lignin chemical structures are known to differ between species, tissues, and regions. The structural heterogeneity of lignin seems to affect its characteristics, and the investigation of such relationship is significant for better utilization of lignin. In present study, the surface properties of lignins were evaluated by inverse gas chromatography (IGC). To compare interspecific difference,

we used a-cellulose coated with milled wood lignin (MWL) prepared from *Pinus densiflora* (Red pine) and *Fagus crenata* (Beech) as sample. By these methods, we determined Lifshitz-van der Waals component of the surface free energy (γs^{LW}) of each lignin samples.

2008-P10

イオン液体 1−*n*-ブチル-3-メチルイミダゾリウムクロライドを用いて処理されたトドマツ（*Abies sachalinensis*）木粉の化学的特徴 ～リグニンと糖の関係に関する考察～

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Chemical characteristics of *Abies sachalinensis* sawdust treated with an ionic liquid, 1-*n*-butyl-3-methyl-imidazolium chloride. Discussion on relationship between lignin and carbohydrate

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Abstract: We investigated chemical characteristics of the insoluble fraction obtained by treatment of *Abies sachalinensis* sawdust with 1-*n*-butyl-3-methylimidazolium chloride ([C$_4$mim]Cl) as one of the ionic liquids (ILs) at 100 and 120ºC for periods ranging from 2 to 24h. Galactose contents in the insoluble fraction increase with as lignin contents increase, whereas other monosaccharide contents except for xylose tend to decrease. These results suggest the existence of lignin bonded closely to galactose in hemicellulose as a structure of lignin-carbohydrate complex (LCC) in *Abies sachalinensis* sawdust.

2008-P11

アカシアファイバーのイオン液体 1-*n*-ブチル-3-メチルイミダゾリウムクロライドへの溶解挙動

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Dissolution behavior of acacia fiber in 1-*n*-butyl-3-methylimidazolium chloride as an ionic liquid

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Abstract: To make the selectively dissolving condition of cellulose in wood components during the dissolution in 1-*n*-buyl-3-methylimidazolium chloride ([bmim]Cl) clear, *Acacia mangium* fiber, milled fiber and wood meal were heated in [bmim]Cl. After the treatment for 24 hours at 100ºC, the yield of residue from milled fiber, fiber and wood meal were 71, 84 and 88%, respectively. The residue from milled fiber treated with [bmim]Cl decreased with increasing temperature and time. In addition, glucose, which is hydrolyzed by the carbohydrate analysis from, wood materials treated with [bmim]Cl decreased rapidly, although their acid insoluble parts increased. The result indicates that the dissolution rate of carbohydrates such as cellulose in wood components is faster than that of lignin.

2008-P12

リグニン分析法のエーテル結合開裂能の評価 ー β-*O*-4 型人工リグニンポリマーの分解性−

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Quantifiability of ether bond cleavage of lignin analysis method -Degradability of β−O-4 type artificial lignin polymer-

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Abstract: Thioacidolysis and nitrobenzene oxidation are methods for analyzing lignin structure by cleavage of aryl ether linkages in lignin. However, the reaction efficiencies of the cleavage to polymeric materials are not clear yet. In this study, we evaluated thioacidolysis and nitrobenzene oxidation reactivity to cleavage of aryl ether linkages, β-*O*-4 linkage in particular, by using the artificial lignin polymer, which was comprised of only β-*O*-4 linkage. The yields of monomeric product by thioacidolysis and nitrobenzene oxidation under the conventional conditions were about 70% and 50%, respectively. These results reveal that these methods incomplete decompose β-*O*-4 macromolecule.

2008-P13

β-O-4 結合の新規な選択的開裂法 ー β-phenoxy sulfone elimination method（β-PSE 法）ー

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New selective stepwise cleavage method for the β-O-4 linkages —β-phenoxy sulfone elimination method—

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Abstract: We develop the new selective stepwise cleavage method for the β-O-4 linkages with a quantitative yield carried out under the mild reaction conditions without any side reactions. This degradation method involves basically three reaction steps: 1) Nucleophilic substitution of the γ-primary or α-secondary hydroxyl group in the β-O-4 structure with inodorous alkylthiol such as $C_{12}H_{25}SH$, 2) Oxidation of the thioether to sulfone, and finally 3) β-Elimination of β-phenoxy sulfone under the mild alkaline conditions*, i.e.*, 0.1N-NaOH to produce α, β-unsaturated sulfone with spontaneous β-O-4 bond cleavage. This method may be useful especially for die elucidation of LCC-structures.

2008-P14

t-BuOK/*t*-BuOH 系におけるリグニン β-*O*-4 結合の挙動

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Behavior of lignin β-*O*-4 bond in *t*-BuOK/*t*-BuOH system

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Abstract: We have focused on *t*-BuOK as a base and investigated the efficiency of the *t*-BuOK/ *t*-BuOH system to cleave β-*O*-4 bond in lignin under mild conditions (0.5 mol/l *t*-BuOK/*t*-BuOH, 30ºC) using lignin model compounds, 2-(2-methoxyphenoxy)-1-(3,4-dimethoxy- phenyl)propane-1,3- diol (VG) and 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethanol (V'G). The results showed that the β-*O*-4 bonds of VG and V'G are certainly cleaved and 2-methoxyphenol is quantitatively detected from both compounds. This is surprising because much severer conditions (*ca*. 2 mol/l NaOH, >150ºC) are commonly required to cleave these bonds in aqueous media. The degradation of both compounds was approximated to pseudo-first-order rate equations, and the rate constants of VG and V'G were 0.0022 and 0.0015 min^{-1}, respectively, which shows the faster degradation of VG than V'G and suggests the contribution of the g-position of VG to this cleavage reaction. However, wood meal was not delignified well and relatively large amounts of carbohydrates were removed when it was treated in the *t*-BuOK/*t*-BuOH system at the elevated temperature. This result suggests that delignification is not controlled only by potential ability to cleave chemical bonds between lignin subunits but by various topochemical factors.

2008-P15

非木質組織のリグニン定量

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Determination of lignin content in non-wood tissues and plants

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Abstract: It has been presumed that Klason method overestimates the lignin content of non-wood tissues or plants, but a method to determine the “true" lignin content of these samples has not been established yet. Our previous studies showed that wood and non-wood are reasonably distinguished by the yields of specific lignin degradation products obtained by nitrobenzene oxidation and ozonation analysis but not by their Klason lignin contents. The yields of these degradation products from non-woods were always lower than a certain level although their Klason lignin content is sometimes extremely high. On the other hand, woods always gave higher values than this certain level. These results suggested that Klason residue obtained from non-woods contain large amount of non-lignin substances. However, one possibility was still remaining; that is the lignin structure of non-wood plants or tissues is rich in condensed type so that these specific degradation products can be given only in small yields. If we can “count” the number of aromatics contained in the Klason residue, we can verify this possibility. For this purpose, we developed a method based on IR absorption and applied to Klason residues of both wood and non-wood samples. It was successfully shown that the number of aromatics in the Klason residue from non-wood was very low compared with that of woods, and it was corresponding well to the low yield of lignin degradation products from non-wood samples. Further research is conducted to elucidate what are included as non-lignin substances in the Klason residue of non-wood samples.

2008-P16

カシノナガキクイムシによる病傷害を受けたコナラ辺材のリグニン構造

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Structure of lignin in the sapwood of *Qurecus serrata* Thunb. infected by *Platypus Quercivora*

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Abstract: When the sapwood of *Quercus serrata* is wounded by an insect of *Platypus Quercivora*, the area surrounding the wounded part is infected by a symbiotic fungi of this insect, *Raffaerea quercivora*, which results in a discoloration of this area. As a defense response of the tree, polymeric substances are secreted at the boundary of this discolored area and normal area. Because these substances are positive to phloroglucinol-HCl colorization reaction, these are often called "lignin-like compounds". In order to analyze the any change caused in lignin structure of discolored area, we prepared samples along several lines that extended to different directions from the center of discolored area, and the change of structure and amount of lignin along these lines were examined. If we can find a clear tendency from the center to outer part beyond the difference of direction, it is reasonably assumed that the change corresponds to the discoloration. According to this strategy, about 20 samples were prepared from different parts in one discolored area, and, Klason lignin determination, nitrobenzene oxidation and ozonation analysis were performed. Even though the difference was not large, a clear tendency was found in the change of Klason lignin content, SN ratio or the total yield of aromatic aldehydes obtained by nitrobenzene oxidation along the lines beyond the difference of direction. We are now looking into in more detail how these difference were created based on the hypothesis that these were initiated by fungal infection.

2008-P17

アカマツ木粉の熱分解生成物の分析～回収留分の定量的検討と熱分解残渣の分析～

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Quantitative analysis of pyrolysis products derived from red pine wood meal "iquid products and pyrolysis residue"

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Abstract: Red Pine wood meals were pyrolysed by tube type kiln under various conditions and quantitative analysis by GC was performed on the main 18 compounds in the fraction recovered as a liquid pyrolyzate. These determined compounds accounted for only about 10% of all liquid pyrolysate.
Determination of water in this fraction by ^{1}H-NMR suggested that 60% of the fraction was water.

2008-P18

泥炭を通過した水中に存在するリグニンの研究

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Lignin in dissolved organic matter obtained from peat swamp water

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Abstract: It is well known that lignin is highly resistant against biological attack. Some part of biologically modified lignin in peat would be expected to dissolve in water. In this study, dissolved organic matters (DOM) isolated from water soaked out of Ishikari (Japan) and To Daeng (Thailand) peat swamps were investigated. Well-defined lignin structural features, *e.g*., products of alkaline nitrobenzene oxidation, methoxyl group, and resonance signals for β-O-4 linkage around 6 ppm in ^{1}H-NMR spectrum, were hardly detected in DOM. Successive treatment consisting of diazomethane methylation and saponincation suggested that DOM has 0.09-0.14 mol/C mol of acidic hydroxyl groups, among which 0.05-0.08 mol/C mol were unstable to alkali when methylated. Average molecular weight of DOM was at MW 1,600. It was considered that lower part of molecular weight of peat in which much of hydrophillic functional group was introduced by biological modification, was dissolved into water. In ^{1}H-NMR spectrum of DOM obtained from Ishikari showed weak but clear peak attributable to aromatic proton.

2008-P19

Spectral study on reaction mechanism of etherification of rice straw

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Abstract: Etherification of rice straw with epoxy chloropropane was carried out at 120ºC for 1-8h in toluene with NaOH as a base. The extent of etherification was estimated by the use of weight percent gain (WPG) as an indication. FT-IR spectroscopy were used to investigate the changes in composition and structure of rice straw that had been subjected to pretreatment and epoxy chloropropane modification. WPG of epoxy chloropropane modified rice straw increased with reaction time. The increase was first significant with the progress of reaction time, and the increment became slight after 5h. FT-IR analyses of epoxy chloropropane modified rice straws agreed with the well established reaction mechanism of epoxy chloropropane. Namely, two -OH groups of rice straw were replaced by two ether links in the former three steps, and one -OH group generated in propane chain derived from epoxy chloropropane in the fourth step.

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2009-101

改変型植物酸性 Peroxidase の酵母での発現と精製(3)

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Heterogeneous expression and purification of modified plant peroxidase (3)
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Abstract: Lignin peroxidase of *Phanerochaete chrysosporium* can oxidize the many environmental pollutants and lignin by assuming Trp-171 near the surface of the enzyme of the catalytic site. CWPO-C that is one of popular POXs can oxidize sinapyl alcohol polymers, and is presumed that Tyr-177 and Tyr-74 exposed to the surface of the enzyme are the catalytic sites. Moreover, the surrounding amino-acid residues of the catalytic sites influenced the specificity of substrates. We introduced the mutations into prxA3a, a POX gene of *Populus kitakamiensis*, to change the corresponding amino acid residues at the positions to Trp residue of Lignin Peroxidase and Tyr residues of CWPO-C and to change the surrounding amino acid residues of the catalytic sites, and examined the changes in the substrate specificities.

2009-102

タバコ・ポプラにおける細胞分裂マーカーcycB pro.:GUS を利用した維管束形成層の細胞分裂評価

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Analyze of cell division on vascular cambium with the marker *cycBpro.:GUS* in tobacco and poplar
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Abstract: The researches about components of cell wall have been investigated with model plants, for example *Arabidopsis thaliana* or *Oryza sativa*. To keep plant biomass sustainably in 21st century, we indicate that the research should be approached with woody plant. Woody plant has vascular cambium, and show thickening growth and a lot of biomass accumulation. We indicated the regulation of cell division on vascular cambium effects beneficial change about plant biomass production. Therefore, we approached analysis about cell number, cell differentiation, and cell wall formation in vascular cambium. In this work, we have made transgenic tobacco and poplar. First, it is overexpressed cell cycle G1/S phase regulated factor, cycD2, E2F, DP, and E2F/DP, and the cambium was enlarged In Only cycD2 transgenic plant. Second, we approached with cell division marker cycB1：3pro.:GUS to check cell cycle regulation. As a result, the activity was not secondary meristem we targeted, but primary meristem.

2009-103

イネをモデルとした植物細胞壁形成過程に関する研究（４）-Glycosyl-phosphatidylinsitol- anchored protein はイネの細胞壁高次構造形成にどのように関わるのか ？－

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Study of plant cell wall formation in *Oryza sativa* L. (4) –How does glycosylphosphatidyl- inositol-anchored protein relate to cell wall conformation in rice plant (*Oryza sativa* L.)? –
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Abstract: Previously, we succeeded in isolating a novel mutant *cwa1*, *bc1* allele of *japonica* species of

rice, which was likely to be loss-of-function mutations of AtCOBL4 ortholog encoding a putative glycosylphosphatidylinositol (GPI)-anchored COBRA family protein and unable to synthesize normal secondary walls. The novel rice mutant *cwa1* has lost a regulation of deposition and assembly of cell wall materials to form the architecture of the even pattern of thickening secondary cell wall in the sclerenchymatous cells of rice internodes. So far, the primary function of AtCOBRA is hypothesized to be orienting cellulose microfibrils, presumably through some sort of interaction with the AtCesA complex and microtubules. One hypothesized way of ahieving this is through the putative carbohydrate binding module (CBM) present on the AtCOB protein. In rice genome, the BC1 gene encodes a plant-specific GPI-anchored COBRA family protein with a putative CBM. In this study, by 3-amino acid substitution in the putative CBM, we examine the function of putative CBM in cell wall formation process through binding to cell wall matrix carbohydrate.

2009-104

イネ CAD 遺伝子変異体 *gh2* の稲わらの糖化効率

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Saccharification degree of lingo-cellulose in rice straw of a cinnamyl alcohol dehydrogenase mutant, *gh2*

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Abstract: We are attempting the alteration of the cinnamate/monolignol pathway to improve bioethanol production from rice straw. In this study, we focused on cinnamyl alcohol dehydrogenase (CAD). CADs are the enzymes that reduce the *p*-hydroxycinnamaldehydes to the corresponding alcohols. The *brown midrib 1* mutant of maize is known to have low activity of CAD and used as forage crop because of its high digestivity. We found a rice mutant having retrotransposon insertion in a CAD gene. It had lower lignin content in all tissues compared to those of control plants. We investigated the enzymatic saccharification of the plants and found higher degree in the mutant.

2009-105

ゴマの抗酸化リグナンであるセサミノールの生合成経路

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Biosynthesis of sesaminol, an antioxidant lignan in *Sesamum indicum* seeds

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Abstract: Sesame seeds contain sesaminol, a phenolic and antioxidant lignan, with sesamin and sesamolin. However, biosynthetic pathway to sesaminol peculiar to the sesame seeds was unknown. To clarify the biosynthetic pathway to sesaminol and the related sesame lignans, isolation and identification of sesaminol, minor sesame lignans, and lignan glycosides from the sesame seeds, and enzymatic formation of sesaminol were carried out. Pinoresinol, piperitol, sesamolinol, 7-episesaminol, and sesamolinol diglucoside were isolated and identified together with sesaminol and sesaminol triglucoside. It was suggested that incubation of sesamin with a microsome fraction from the sesame seeds gave sesaminol.

2009-106

Phanerochaete chrysosporium のリグニン分解酵素発現におけるカルモデュリン阻害剤の影響

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Effect of calmodulin inhibitors on the production of ligninolytic enzymes in *Phanerochaete chrysosporium*
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Abstract: Our previous study revealed that the calmodulin (CaM) gene was upregulated during initiation of lignin peroxidases (LiPs) and manganese peroxidases (MnPs) production in *Phanerochaete chrysosporium*. In this study, we investigated effects of CaM inhibitors, trifluoperazine (TFP), W-7 and W-5 on the enzymes production in *P. chrysosporium* to confirm the role and involvement of CaM in the enzyme expression. When the chemicals were added into reaction mixtures including the crude enzymes, W-7 and W-5 didn't influence the enzyme activities, but, unexpectedly, TFP specifically inhibited LiP reaction. When 100 7M of W-7 was added into the fungal culture within 72 h of the culture start, the enzyme expression was inhibited. Using a contrast medicine, W-5 instead of W-7, about 50% of the enzyme activities were still observed, which indicates that the inhibition mechanism of W-7 was interaction with CaM. Real time RT-PCR analysis revealed that 12 genes of LiPs and MnPs were transcribed parallel with the enzyme activities under the culture condition and the all genes were inhibited by W-7 at transcription level.

2009-107
土壌から単離した菌類によるクリセンの分解
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Degradation of chrysene by a fungus isolated from soil
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Abstract: Chrysene, a polycyclic aromatic hydrocarbon (PAH), is an important class of environmental pollutants because it has been found to have a variety of toxic, mutagenic, and resist biodegradation. The degradation of chrysene in a liquid medium by a fungus isolated form soil is studied. A single strain fungus was found for the best ability to degrade chrysene in an agar medium. This fungus, *Fusarium* sp. F092, was tested to degrade chrysene in both saline and non-saline conditions. Effects of surfactant concentration and agitated culture were also conducted to improve the fungus ability for degradation of chrysene. Salinity level of sea water (35o/oo) had no significant effect on the degradation of chrysene in both on solid and liquid media. The degradation of chrysene in a liquid medium had improved 1.5 folds when the culture agitated at 120 rpm. Several non- ligninolytic enzymes secreted by a fungus were detected in a liquid medium. The highest activity of 1,2- dioxigenase reached 203.5 Ul-1 on 30 days and 29.7 Ul-1 for 2,3-dioxygenase on 40 days. These results show that *Fusarium* sp. F092 is a potential fungus for bioremediation.

2009-108
白色腐朽菌 Phlebia 属菌による有機塩素系農薬の処理
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Biodegradation of organochlorine pesticides by white rot fungi, *Phlebia* genus
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Abstract: The organochlorine pesticides, dieldrin and heptachlor were used as substrate for degradation experiment by 20 white rot fungi belonging to *Phlebia* genus. *Phlebia acanthosystis*, *Phlebia brevispora* and *Phlebia aurea* were selected based on the degradation ability of dieldrin. Dieldrin was biotransformed to hydroxyl dieldrin and several unidentified metabolites by *Phlebia acanthosystis*, *Phlebia brevispora* and *Phlebia aurea*. Heptachlor was degraded rapidly by almost all of white rot fungi belonging to *Phlebia* genus. The degradation rate of heptachlor was higher than that of dieldrin. Heptachlor epoxide, 1-hydroxychlordene and 1-hydroxy-2,3-epoxychlordene were detected as metabolites from the cultures treated by most of *Phlebia* fungi.

2009-109
DDT degradation potential of mushroom waste medium
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Abstract: *Pleurotus ostreatus* (Hiratake) had high ability to degrade and mineralize DDT (1,1,1-trichloro 2,2 bis (4-chlorophenyl) ethane) in potato dextrose broth (PDB) medium. *P. ostretaus* also degraded DDT in solid medium higher than *Gloeophyllum trabeum* and *Phanerochaete chrysosporium*. *P. ostreatus* medium before and after mushroom production (waste medium) were used and compared. DDT was degraded 23% and 31% during 4 weeks incubation by *P. ostreatus* medium before and after mushroom production, respectively. Mineralization of ^{14}C-DDT was also investigated. ^{14}C-DDT was mineralized 3.2% and 3.4% during 4 weeks incubation by *P. ostreatus* medium before and after mushroom production, respectively. It indicated that waste medium was more effective to degrade DDT. For application purposes, degradation potential in artificial DDT-contaminated soil was also investigated. The waste medium of *P. ostretus* degraded DDT 40% and 60% during 4 weeks incubation in sterile and un-sterile soils, respectively. DDD (1,1-dichloro-2,2 bis (4-chlorophenyl) ethane) was detected in un-sterile soil, indicated involvement of soil microorganisms. ^{14}C-DDT was mineralized 3.0% and 4.1% in sterile and un-sterile soil, respectively. These results indicated that mushroom waste medium of *P. ostreatus* is the potential nature source which can be used for bioremediation of DDT.

2009-110
イオン液体 1-*n*-ブチル-3-メチルイミダゾリウムクロライドに対する木材構成成分の反応性
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Reactivity of wood components against an ionic liquid 1-*n*-butyl-3-methylimudazolium chloride
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Abstract: Japanese red pine (*Pinus densiflora*) and Japanese beech (*Fagus crenata*) woods were treated with one of ionic liquids: 1-*n*-butyl-3-methylimidazolium chloride. *P. densiflora* dissolved more rapidly compared to *F. crenata*, but its tendency was reversed at the end of treatment for 24 hours. After the treatment at 120ºC for 72 hours, approximately 70% of glucan in *Acacia mangium* fibers was denatured. Although cellulose was dissolved by the treatment at 120ºC for 24 hours, the residue of *A. mangium* fibers kept containing a lignin-carbohydrate complex (LCC). The structure of LCC was estimated a complex of β–*O*-4 type structural element and xylan. We synthesized an LCC model compound with veratrylglycerol-β–syringyl ether and methyl-β-D- xylopyranoside to clarify the stability of LCC during the ionic liquid treatment.

2009-111
イオン液体/DMSO 混合溶媒系に於けるリグニンモデル化合物の分解挙動
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Decomposition of a β-O-4 type lignin model compound in the mixed solvent system of ionic liquid and DMSO
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Abstract: Structural stabilities of phenolic β-O-4 lignin model compounds in the mixed solvent system of ionic liquid and DMSO (IL/DMSO) were examined. Decomposition rate of the model compound, threo-guaiacylglycerol-beta-guaiacyl ether (T-GG), in IL was not significantly affected by the incorporating of 90% of DMSO. However, decomposition of T-GG became gradually slow, if more than 95% of DMSO was incorporated to IL. Enol-ether, one of the primary decomposition products of GG, was also detected in the T-GG decomposition in the IL/DMSO, even in the mixed solvent having very low content of IL (IL/DMSO=0.25/99.75 w/w), although EE was not formed in the pure DMSO. This result suggested that decomposition mechanism of T-GG in pure DMSO was different from that in IL/DMSO.

2009-112
アルカリ処理オゾン酸化クラフトリグニンとアルミニウムとの錯体形成
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Formation of a complex with aluminum by ozone-treated kraft lignins and their low molecular weight fragments
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Abstract: The formation of a complex with aluminum by low molecular weight compounds and saponified ozone-treated kraft lignins was evaluated based on the decrease in pH of their solutions on the addition of 0.1 M $AlCl_3$. Decreases in pH were observed with the solutions containing compounds having adjacent carboxyl groups (oxalic acid), carboxyl/alcoholic hydroxyl groups (glycolic acid), carboxyl/formyl groups (glyoxylic acid), and phenolic hydroxyl groups (protocatechuic acid) on the addition of 0.1 M $AlCl_3$. The malonic and phthalic acids, having two carboxyl groups, were also effective. These results show that the compounds were effective in forming complexes with aluminum. This finding corresponds to the fact that aluminum toxicity is reduced by formation of a complex with aluminum, except in phthalic acid. The chemical structures stated above in ozone-treated kraft lignins contribute, at least partly, to the complex with aluminum. The pH of solutions containing saponified ozone-treated kraft lignins and alkaline-treated kraft lignin decreased more than that without modified kraft lignins on the addition of 0.1 M $AlCl_3$, showing that they were effective in forming a complex with aluminum.

2009-特別講演

木材腐朽菌の新たな機能を求めて ー 環境浄化と健康増進 ー

近藤隆一郎
九州大学大学院農学研究院

Invited Lecture: New functions of wood-rotting fungi -Bioremediation and functional food-

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Faculty of Agriculture, Kyushu University, Fukuoka, Japan

Abstract: Environmental pollutants are a serious concern worldwide because of the hazards they pose to the health of humans and animals. One method that has become increasingly popular for decontamination of the environment has been bioremediation. One of the early reports indicated that lignin-degrading white-rot fungi, as exemplified by *Phanerochaete chrysosporium*, can degrade an extremely diverse group of environmental pollutants. For thousands of years, mushrooms have been known as a source of medicine. In East Asia, the fruiting body of the fungus *Ganoderma lucidum* has been used for centuries. In this presentation, new functions of wood-rotting fungi, bioremediation and functional food, will be discussed.

2009-201

非木質組織のリグニン定量

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On the determination of lignin content in non-wood tissues and plants

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Abstract: In previous studies it was clarified that as Klason residue of non-woody tissues contain definite amounts non-lignin substances, Klason method overestimates the lignin content of non-wood tissues or plants. To see the effect of various kind of extraction to lignin measurement, 9 kinds of extractions were carried to ginkgo leaf and zelkova leaf. After pre-extraction, amounts of lignin measured by Klason method and acetyl bromide method were lower than those of non-extracted samples in most case. But it is not sure whether we can use these extractions to other species.

2009-202

アシドリシスにおいて酸の種類が及ぼすリグニン β-O-4 結合開裂機構への影響について

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Effect of kind of acid on the mechanism of the β-O-4 bond cleavage during acidolysis

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Abstract: In the acidolyses of veratrylglycerol-*β*-guaiacyl ether (VG) using HBr, guauachol (G) was quantitatively produced on the disappearance of VG, but the formation of a Hibbert's ketone, 1-hydroxy-3-(3,4-dimethoxyphenyl)propan-2-one (HK), started after certain lag time and was not quantitative.

In the HCl system, both G and HK were quantitatively produced. In the H2SO4 system, another Hibbert's ketone, 3,4-dimethoxyphenylacetaldehyde (HK'), was fairly produced with the quantitative formation of G, but only trace amount of HK was detected. By the addition of KBr to the HBr system, the disappearance rate of VG was not affected, but the formation of HK as well as G became quantitative. The addition of KCl to the HBr system did not affect the disappearance rate of VG, but the difference in the formation rates between G and HK become smaller than that in the HBr system without KCl. The addition KBr to the HCl system enhances the disappearance rate of VG and formation rate of G. Consequently, the formation rate of HK was slower than G in this case. In all these cases, the formation of G was almost quantitative, but the reaction rate and probably the reaction mechanisms themselves are greatly affected by the kind and amount of counter anion of the acid.

2009-203

レーザー脱離イオン化法によるリグニンの質量分析

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Mass spectrometry of lignin by laser desorption/ionization

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Abstract: Synthetic and natural lignins were analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) and a matrix free-LDI- MS method, named nano-assisted laser desorption/ionization time-of-flight mass spectrometry (NALDI-TOF MS). In the analysis of MALDI with 2,5-dihydroxybenzoic acid as a matrix, peaks originating from various lignin samples, such as, dehydrataion polymer (DHP), β-*O*-4 type artificial lignin and MWL (milled wood lignin) were detected with high reproducibility. MALDI mass spectra of β-*O*-4 type artificial lignin were obtained in a high molecular weight area (over m/z 5,000). Close similarity was found between NALDI-MS and MALDI-MS of the lignins. The soft LDI method is useful for the structural analysis of lignin.

2009-204

p-ハイドロキシフェニル核をビフェニル骨格に有する新規ジベンゾジオキソシン構造

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Novel dibenzodioxocin structures involving *p*-hydroxyphenyl units on their biphenyl units

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Abstract: Cross-coupling of monolignols with biphenyl compounds consisting of *p*-hydroxyphenyl (H) and/or guaiacyl (G) moieties, using Ag_2O, formed dibenzodioxocins. HH-, GH-, and GG-biphenyl types of dibenzodioxocins were found HSQC spectra of H-enriched lignins isolated from C3H deficient alfalfa. Of the three types, the GH-biphenyl type was a major structure. When a GH-biphenyl unit is etherified by 4-O-coupling with another monomer only a single regioisomer is observed – that in which the G-unit is etherified. The other regioisomer β-O-4-linked on the H unit was not found either in the lignin or in the cross-coupling products.

2009-205

マイクロ波増感触媒反応を利用したバイオリファイナリーシステムの開発

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Development of biorefinery system using microwave-sensitized catalytic reaction system

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Abstract: Recently, increase in oil price caused by fossil fuel depletion and global warming by use of the

fuel become serious problem. Therefore bioethanol production from wood, which is the most abundant biomass and distributed worldwide will be developed as an alternative energy resource. Usually sugars obtained from biomass were utilized effectively as resource of many chemicals and polymers. On the other hand, lignin, the second abundant natural polymer has often been burned or discarded without use for chemical resources. Therefore we stated to develop environmentally- benign lignobiorefinery system using microwave-sensitized catalytic reactions.

2009-206

半流通型加圧熱水処理におけるブナリグニンの挙動

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The behavior of lignin in Japanese beech as treated by semi-flow hot-compressed water

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Abstract: Japanese beech (*Fagus crenata*) wood was treated by two-step semi-flow hot-compressed water (the first step: 230ºC/10MPa/15min and the second step: 270ºC/10MPa/ 15min). To study a behavior of lignin during the treatment, water-soluble portion and residue were fractionated and Klason lignin, acid-soluble lignin and alkaline nitrobenzene oxidation products were determined. As a result, about 17wt% on wood basis (64wt% on lignin basis) was found as lignin in water-soluble portion at the first step, while about 4wt% (13wt% on lignin basis) at the second step. In the residue, at the end of the second stage, only 3% of lignin (11wt% on lignin basis) was found. Interestingly, the lignin structures in these fractions were different.

2009-207

スギの半流通型2段階加圧熱水処理におけるスギリグニンの分解

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Decomposition of lignin in two-step semi-flow hot-compressed water treatment of Japanese cedar

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Abstract: Japanese cedar (*Cryptomeria japonica*) was treated by two-step semi-flow hot-compressed water (230ºC/10MPa/15min and 280ºC/10MPa/30min), and fractionated into water-soluble portion, precipitates and hot-compressed water-insoluble residue. The water-soluble portion was then extracted by ethyl acetate to obtain ethyl acetate-soluble portion. For the obtained ethyl acetate-soluble portion and precipitates, consisting mainly of lignin-derived products, gel permeation chromatography (GPC) and gas chromatographic-mass spectrometric (GC-MS) analyses were conducted. As a result, GPC analysis revealed that the ethyl acetate-soluble portion contained lignin-derived monomeric, oligomeric and polymeric products, while the products with relatively higher molecular weight were found in the precipitates. GC-MS analysis of the ethyl acetate-soluble portion, on the other hand, elucidated that β-O-4 ether linkage of lignin as well as C_β/C_γ and C_α/C_β linkages in the propyl sidechain of the C6-C3 units could be cleaved under the condition of hot-compressed water treatment. In addition, the alkaline nitrobenzene oxidation analysis showed a decrease in oxidation products of the hot-compressed water-insoluble residue. This observation clearly confirmed that the cleavage of the ether linkage of lignin was preferably taken place in the present hot-compressed water treatment.

2009-208

木材熱分解における針葉樹、広葉樹リグンの挙動

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Pyrolysis behaviors of softwood and hardwood lignins in wood pyrolysis

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Abstract: Pyrolysis behaviors of Japanese cedar (*Cryptomeria japonica*, a softwood) and Japanese beech (*Fagus crenata*, a hardwood) milled wood lignins were studied with thermogravimetry (TG) and pyrolysis in an ampoule reactor (N_2/600ºC/40-600s). Guaiacol and syringol were also used to understand the behaviors of the guaiacyl- and syringyl-types of aromatic rings in lignin, respectively. As a result, the following results were obtained; 1) DTG peak temperature: lower in beech, corresponding to the low-temperature shoulders of cedar and beech wood samples, 2) devolatilization efficiency: beech > cedar, 3) coke formation: beech > cedar, 4) tar composition: similar after long heating time. Some of these features are explained with the different pyrolysis behaviors of guaiacol and syringol.

2009-209

Relationships between hemicellulose composition and lignin structure in hardwoods

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Abstract: The composition and the absolute amount of neutral sugars were determined for 48 hardwood species (including 17 hardwoods of genus Acacia, 14 hardwoods of genus Eucalyptus and l7 hardwoods of different other genus) by aldito1-acetate method, and their relationships to the syringyl ratio (S/(S+V)) of lignin, which was determined by nitrobenzene oxidation, was investigated. It was suggested that it is hemicellulose but not cellulose that changes with certain tendency in the conjugation with the change of lignin structure. The relationships between syringyl ratio and characteristic peak area ratios of aromatic ring in IR spectrum were also studied.

2009-210

炭水化物 C-2 位に対する活性酸素種の反応性の評価

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Evaluation of the reactivity of active oxygen species toward the C-2 position of carbohydrate

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Abstract: The reactivity of active oxygen speices (AOS) toward carbon-hydrogen bonds at the C-2 positions of carbohydrate was examined using methyl β-D-glucopyranoside (MGP), methyl β-D-mannopyranoside (MMPβ), and methyl β-D-(2-^{2}H)glucopyranoside (MGPβ-2D). In this study, AOS were *in situ* generated by subjecting phenolic compounds, 2,4,6-trimethylphenol (TMPh) and 4-hydroxy3-methoxybenzyl alcohol (vanillyl alcohol, VA), to the oxygen oxidation. MMPβ was degraded greater than MGPβwhen they were treated together in the presence of each phenolic compound, which suggests that the stereo configurational difference in their C-2 positions has a certain effect on their reactions with AOS. The degradations of the carbohydrate model compounds

seemed to be slightly but clearly dependent on kind of AOS origin. In the absence of the phenolic compounds, MMPβwas degraded slightly in the oxygen alkaline treatment although MGPβ was stable in the same system, suggesting that the stereo configuration at the C-2 position has an influence on the lability to oxygen oxidation.

2009-211

Dissolution of ethylenediamine pretreated high kappa pulp in LiCl/DMSO

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Abstract: Various hardwood and softwood chemical pulps, including those with relatively high lignin content (up to ca.10.5%), were completely dissolved without milling in LiCl/DMSO after a pretreatment with ethylenediamine (EDA). Because the milling of the sample is not required, degradation of cell wall components caused by milling does not take place. After the EDA pretreatment, the crystallinity of pulps were found to be kept as high as the corresponding original pulps although the crystal structure was changed. It is the first time that transparent solutions of underivatized pulps with high lignin content were obtained in a simple organic solvent system. Formation of pulp-EDA complex with proper EDA ratio seems to be critical for the dissolution in LiCl/DMSO. The NMR spectrum of EDA treated pulp solution provided good resolution even though the DP of cellulose in the pulp is very high.

2009-212

ポリサルファイド蒸解と修正蒸解の最適な組み合わせに関する検討

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科

Application of new cooking system using highly concentrated polysulfide to modified cooking with multi charges of cooking liquor

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Abstract: Polysulflde cooking is one of the most efficient technologies to increase pulp yields. The polysulfide has to be produced from white liquor (WL) to keep the Na^+ and S^{2-} balance in the WL recovery cycle. When we try applying the polysulfide to iso-thermal cooking (ITC), not only NaOH but also Na_2S at a start of the cooking are diluted by sequential charges of cooking liquor. Therefore, a new electrolysis method of WL has been developed to produce the polysulfide efficiently. In this study, the combinatorial use of ITC and polysulfide cooking were evaluated, expecting a process in which the mill scale pilot electrolyzers were installed.

2009-213

硫酸リグニンを原料としたポリエステルの合成

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Synthesis of polyester using sulfuric acid lignin

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Abstract: In this study, polyesters were synthesized using sulfuric acid lignin. First, sulfuric acid lignin was converted into water-soluble polymer (HSAL) by hydrothermal reaction under alkali condition. H-SAL was introduced carboxyl group during the hydrothermal reaction and the acid-type HSAL (-COOH) could be dissolved into ε-caprolactone. The polyesters were synthesized using the acid-type H-SAL andε-caprolactone with varying ratio of them. The prepared polyesters with high H-SAL content exhibited the swellability in organic solvent. The thermal properties of the prepared polyesters were measured by DSC. From the results, an endothermal peak, which corresponds to the crystalline fusion of the polycaprolactone (PLA) segment was shifted at lower temperature and the area was smaller with increase the H-SAL content in the polymer.

2009-214

リグノスルホン酸/ピロリドン環含有ポリマー複合体の調製と吸着機能材料としての応用

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Preparation of lignosulfonic acid/polymer containing pyrrolidone rings and application to absorbents

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Abstract: In order to utilize lignosulfonic acid (LSA) as absorbents of bio-related substances, LSA-containing composites were prepared by (a) immersion of polyvinylpolypyrrolidone or cellulose acetate (CA)/poly(N-vinyl pyrrolidone) (PVP) complex in a LSA solution and (b) re-precipitation from a solution of CA/PVP/LSA mixture. Chemical compositions of the products were successfully determined by FT-IR measurements. LSA was effectively incorporated into the composites via hydrogen bonding with vinylpyrrolidone unit. An adsorption property of the composites to catch nicotine was evaluated with Freundlich and Langmuir models, revealed the occurrence of a strong interaction between LSA and nicotine especially in the composites prepared by (a).

2009-215

リグニンスルホン酸塩及び芳香族エポキシ化合物を原料とするエポキシ樹脂の合成と熱的性質

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Synthesis and thermal properties of epoxy resins derived from sodium ligninsulfonate and aromatic epoxy compound

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Abstract: Sodium ligninsulfonate (LS) was dissolved in ethylene glycol (EG) and the obtained mixture was allowed to react with succinic anhydride in order to obtain a mixture of ester-carboxylic acid derivatives (LSEG polyacid, LSEGPA). EGPA was also synthesized from EG. LSEGPA was allowed to react with phthalic acid diglycidyl ester (PhADGE) in the presence of a catalytic amount of dimethylbenzylamine to form epoxy resins. The molar ratio of epoxy groups to carboxylic acid groups ([EPOXY]/[ACID] ratios, mol/mol) was maintained at 1.0. The contents of LSEGPA in the mixture of LSEGPA and EGPA (LSEGPA content) were varied from 0 to 100 %. Thermal properties of epoxy resins were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG). Glass transition temperatures (T_g's) of epoxy resins increased with increasing LSEGPA contents, suggesting that lignin acts as a hard segment in epoxy resin polymer networks. Thermal decomposition temperatures (T_d's) of epoxy resins were almost constant regardless of LSEGPA contents.

2009-216

リグニン由来エポキシ樹脂の合成とその応用

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Synthesis of lignin-derived epoxy resin and its application

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Abstract: We have tried to apply epoxy resin derived from woody lignin to copper-clad laminates and printed-circuit boards. Lignin (L) and lignophenol (LP), which was lignin derivatives extracted by phenol from wood, were successfully converted to organic-solvent-soluble epoxidized-lignin (EL) and epoxidized-lignophenol (ELP) by using tetramethyl ammonium hydroxide. EL and ELP as epoxy resins, L and LP as hardeners were applied to copper-clad laminates. Glass transition temperatures of lignin-derived epoxy resin hardeners were over 200 degrees C, and higher than those of commercially available epoxy resin hardeners that were derived from oil. The properties of copper-clad laminates using lignin-derived epoxy resin hardeners were almost the same as those of commercially available laminates.

2009-P01

豪雪地帯に生育する樹木の根元曲がり材の主成分について

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Chemical composition of basal bending wood in heavy snowfall region

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Abstract: Basal bending of trees was formed by snow pressure in the snowfall region. We analyzed chemical composition of normal and basal bending Sugi (*Cryptomeria japonica* D.Don) wood. As a result, lignin contents of basal bending wood were higher than normal wood, holocellurose contents of normal wood were higher than basal bending wood. In eccentric thickening growth part of basal bending wood, range of lignin and holocellulose contents were similar to normal wood. It was suggested that the basal bending part, except compression wood, was normal type growth.

2009-P02

ハンゲショウにおける 9,9’-デオキシ型ネオリグナンおよびリグナンの立体化学と生合成

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Stereochemistry and biosynthesis of 9,9’-deoxy-neolignans/lignans by *Saururus chainensis*

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Abstract: 9, 9’-Deoxy-lignans/neolignans have been isolated and identified in mainly Myristicaceae or Lauraceae plants. However, their biosynthesis is unknown. The present report describes stereochemistry and biosynthesis of Δ8’-4,7-dihydroxy-3,3’-dimethoxy-8-*O*-4’-neolignan, whose *erythro* and *threo* isomers are named as Machilins C and D, respectively, in Saururus chainensis, that is, (1) dehydrogenative polymerization of isoeugenol with horseradish peroxidase and H2O2 (*erythro* : *threo* = 16 : 84), (2) isolation of the 9,9’-deoxy-8-*O*-4’ neolignans from the root of S. chainensis (4 : 96), (3) dehydrogenative polymerization of isoeugenol with a cell-free extract from *S. chainensis* and H_2O_2 (14 : 86). The diastereomeric ratios of the 9,9’-deoxy-8-*O*-4’-neolignan are shown in parentheses. A peroxidase activity in *S. chainensis* gave Machilin C and Machilin D, but the ratio of the latter to the former is the same as the case in horseradish peroxidase (1). However, the ratio in the neolignan from the plant (3) is larger than the above ratios in (1) and (2). Therefore, the presence of a specific Machilin D synthase was suggested.

2009-P03

シラカンバ No. 8 幼植物体におけるカバノアナタケ菌 IO-U1 株感染部位縦断面でのフェノール性化合物の堆積及びペルオキシダーゼ活性の経時変化

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Time-course changes in accumulation of phenolic compounds and peroxidase activity in the longitudinal sections from *Betula platyphylla* var. *japonica* No. 8 plantlets infected with *Inonotus obliquus* IO-U1 strain

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Abstract: It is well known that *Inonotus obliquus* is a fungas causing canker disease of birch trees. Purpose of this study is to clarify the defense mechanisms of *Betula platyphylla* plantlets against infection with *I. obliquus*. Time-course changes in accumulation of phenolic compounds and peroxidase activity were observed in the longitudinal sections from birch plantlets. The accumulation of phenolic compounds and peroxidase activity were found in both wounded and infected plantlets, especially they were prominent in the infected plantlets. In the infected plantlets, the accumulation of phenolic compounds and peroxidase activity were observed in the vessels located above and below the infected portion. These results suggest that phenolic compounds might be polymerized by the peroxidases, forming barrier to protect the vessels from invasion of the fungal hyphae.

2009-P04

木材腐朽担子菌におけるシトクロム P450 分子種の多様性

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The diversity of cytochrome P450 of wood-rotting basidiomycetes

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Abstract: We explored the molecular diversity of cytochrome P450 (P450) in the brown-rot fungus *Postia placenta* using bioinformatic and experimental approaches. Based upon bioinformatic survey, 325 putative coding sequences of cytochrome P450s were discovered from the genome database. To facillitate molecular and functional diversities of *P. placenta* P450s (PpCYPs), we attempted to isolate and characterize cDNAs using RT-PCR. To date, we confirmed the gene expression of 157 PpCYPs and cloned 123 PpCYPs as full-length cDNAs encoding a mature open reading frame. In addition, phylogenetic analysis was done suggesting that white-rot and brown-rot basidiomycetes have been developed through vigorous evolution of P450s to meet their unique metabolic diversities.

2009-P05

高活性リグニン分解菌 *Phanerochaete sordida* YK-624 株リグニン分解関連酵素遺伝子のクローニング及び発現解析

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Cloning and transcriptional analysis of genes which are involved in the lignin degradation by *Phanerochaete sordida* YK-624

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Abstract: Genes of 5-aminolevulinic acid synthase (ALAS) and 1,4-benzoquinone reductase (BQR) were cloned from hyper lignin-degrading fungus *Phanerochaete sordida* YK-624. ALAS gene from *P. sordida* YK-624 (*PsALAS*) showed highest identity (93.0%) with ALAS from *Phanerochaete chrysosporium* ME-446. BQR gene from *P. sordida* YK-624 (*PsBQR*) showed highest identity (93.1%) with the predicted BQR cording gene in genomic sequence of *P. chrysosporium* RP78 which has been named as e_gwh2.5.446.1. The expression of *PsALAS* showed significant correlation with the production of ligninolytic peroxidases such as manganese peroxidase and lignin peroxidase. The expression of *PsBQR* was strongly induced by the addition of vanillin.

2009-P06

The enhancement of cellulose saccharification in corn stover by pretreatment with brown-rot fungi

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Abstract: *Gloeophyllum trabeum* KU-41 was chosen for corn stover pretreatment for bio-ethanol production. Alditol acetate method was used to determine the changes of sugar content in corn stover pretreated by *G. trabeum* KU-41. The content of xylan has been decreased by 25% in comparison to the control. For cellulose crystallinity determination by X-ray diffraction, the crystallinity in corn stover pretreated didn`t change significantly compared to the control. The activity of xylanase secreted by *G. trabeum* KU-41 was much higher than that of other *G. trabeum* strains. Xylan was degraded and hemicellulose might be disentangled during the pretreatment

2009-P07

パラコッカス属細菌による黒液リグニンの分解と分解産物の定性

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Biodegradation of black liquror lignin and identification of degradation products by *Paracoccus*.sp.

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Abstract: In this study, we isolated a lignin degradation bacterium from IBIDEN activated sludge. The bacterium was identified as *Paracoccus* species by the 16s rDNA genetic analysis. *Paracoccus* sp. was degraded black liquor lignin to some products with a liquid shaking culture for 7 days at 30℃. Low molecular aromatic compounds such as salicylic acid, 2,3-dihydroxybenzoic and 3,4-dihydroxybenzoic acid were detected in a bacterium treated sample with GC/MS. In our results, there is a possibility of efficiency biotechnology refinery of black liquor lignin by bacteria.

2009-P08

白色腐朽菌由来の粗酵素を用いたアゾ染料の分解

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Degradation of azo dyes with a crude enzyme from white rot fungi

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Abstract: To purify effluents from textile industries and so forth, degradation of three azo dyes, Reactive Red 4 (RR4), Reactive Black 5 (RB5) and Reactive Green 19 (RG19) by a crude enzyme from a white-rot fungus, PL1 was conducted. Degradation rate of the dyes by the enzyme was about 10 to 20%. To enhance the degradation rate, effects of pH, hydrogen peroxide and manganese sulfate concentrations, and mediators on degradation of the dyes were investigated. Using the optimum reaction conditions found, degradation of the dyes by the enzyme was further conducted. It was found that 90 to 95% of each dye could be degraded for within 24 hours by the enzyme.

2009-P09

白色腐朽菌由来の酵素による1-ニトロピレンの分解

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Degradation of 1-nitropyrene by enzymes from white rot fungi

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Abstract: Nitropolycyclic aromatic hydrocarbons (NPAHs) are a widely distributed class of environmental contaminants which can be formed in the atmosphere by reaction of nitrogen oxides with polycyclic aromatic hydrocarbons. In the present study, 1-nitropyrene, one of NPAHs was treated with each two ligninolytic enzymes, laccase (Lac) and manganese peroxidase (MnP) prepared from the culture of white rot fungi. The Lac-HBT (1-hydroxybenzotriazole) system in the presence of Tween 80 decreased 1-nitropyrene by 30% after 24 h of treatment, however, Lac-HBT system in the presence of Tween 20 did it only by 10%. On the other hand, MnP in the presence of Tween 80 (MnP-Tween 80) decreased 1-nitropyrene by 50% after 24 h of treatment. These results indicate that, among the three enzymatic treatments, MnP-Tween 80 is most effective in removing 1-nitropyrene.

2009-P10

Separation of wood cell components by the use of two dissolving procedures, "ball-milling and dsdsolution in LiCl/DMSO" and "EDA-treatment and dissolution in LiCl/DMSO"

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Abstract: The different fractions of wood cell components were separated by the dissolution of wood meal in lithium chloride/dimethyl sulfoxide (LiCl/DMSO). By putting milling pretreated wood meal in to DMSO containing different amount of LiCl, series of soluble fractions and residual fractions can be obtained. The lignin in the residual fractions has always higher syringyl ratio (S/(S+V)) and higher yield of nitrobenzene oxidation products (S+V) than that of corresponding soluble fractions. However, lignin in the soluble fractions, which was separated from ethylenediamine (EDA) pretreated wood meals had more non-condensed type than residual fractions. Both the yield of S+V and the ratio of S/(S+V) of soluble fraction from EDA pretreated wood were higher than those of residual fraction. Characteristic carbohydrates found in the most difficult parts to be dissolved in milling pretreated wood meals were hemicelluloses rather than cellulose. Contrary, the weight ration of xylose was relatively higher in soluble fraction than residual part separated from EDA pretreated wood meals.

2009-P11

フリーラジカルによるリグニンモデル化合物の反応部位に関する研究(2)

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Study on reactive position of lignin model compounds with free radicals (2)

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Abstract: A white rot fungus, *Ceriporiopsis subvermispora* degrades lignin by radical reactions of low molecular mass metabolites at a site far from enzymes. As a possible ligninolytic system by the fungus, in situ radical reactions have been proposed. Our previous experiments clearly indicate that carbon-centered (CR) and alkoxyl (AR) radicals degrade non-phenolic lignin model compounds (LMCs) through hydrogen Abstraction at benzyl position of LMC, but peroxyl radical (PR) does not. Furthermore, direct detection of free radicals using ESR support this reactivity of AR with LMCs. In the present study reactivity and LMC degradation mechanism of CR produced from azo-compounds was analyzed by UV-ESR method.

2009-P12

tert-ブトキシドを塩基とする反応系における β-O-4 結合開裂機構の検討

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Investigation into the mechanism of the β–O-4 bond cleavage in a reaction system using tert-butoxide as a base

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Abstract: The β-O-4 bond cleavage of dimeric non-phenolic lignin model compounds, 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethanol (2), 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethanone (3), and 1-methoxy-2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl) ethane (4) was examined in a potassium *tert*-butoxide/*tert*-butanol ($KO^tBu/^tBuOH$) system. The β-O-4 bonds of (2) and (3) cleaved in 0.5 mol/l KO^tBu at 30ºC, which were much milder than those in general alkaline based pulping processes. The disappearance of (3) was much faster than (2), which was similar to the results in aqueous NaOH system reported by Gierer. An oxidized product, 3,4-dimethoxybenzoic acid (6), was detected, which is a characteristic in this reaction system. The β-O-4 bond of (4) did not cleave in the same system, indicating that the initial reaction of (2) is the dissociation of the α-hydroxy group induced by $^-O^tBu$.

2009-P13

ヨウ化アルミニウム(III)試薬によるリグニン高分子モデル化合物の低分子化

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Depolymerization of a lignin polymer model compound with aluminium iodide (III)

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Abstract: Aluminium iodide (III), an effective reagent for cleavage of low-molecular-weight alkyl-aryl ethers, was used to observe if it was able to cleave and depolymerize a lignin polymer model compound consisting of guaiacyl units exclusively with β-O-4 linkages. The AlI_3 reagent degraded the lignin polymer model compound to give some low-molecular-weight compounds, one of which was increasing in peak intensity (in total ion chromatogram) with increasing AlI_3 Charge ratio and reaction time. The reagent, however, did not cleave all the β-O-4 linkages of the lignin polymer
model compound as it did those of a lignin dimer model compound.

2009-P14

スギ針葉中のリグニン −DFRC 法による分析の試み−

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Detection of lignin in sugi leaves —An attempt of DFRC analysis—

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Abstract: Many questions are left in lignins of tree leaves and needles, beginning with in their occurrence, structure and functions. The Klason method often gives excessive results because of insoluble contaminants. In this study, DFRC (Derivatization Followed by Reductive Cleavage) method, that can degradate the arylether structure in lignin selectively, was employed to sugi (*Cryptomeria japonica*) leaves. This method gave the lignin-specific C6-C3 degradation products from sugi leaves, that show the existence of lignin in leaves.

2009-P15

β-O-4 結合の新規な選択的開裂法:β–PSE 法の検討(1) −開裂条件の最適化−

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Studies on new selective cleavage method for β-O-4 linkages of lignin (β-PSE method) (1)
—Optimization of mild alkali cleavage reaction condition—

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Abstract: New selective β-O-4 cleavage method (named β-PSE method) which consisted of four reactions has been proposed. In this study, the final reaction (dilute alkali cleavage) of G-type lignin dimer was investigated to determine its optimum conditions. The yield of degradation product reached a peak after 1~3 h and decreased, and it was significantly affected by reaction temperature. As a result, the yield was maximum in the conditions (NaOH concentration:0.03N, temperature:25℃, reaction time:1.5h). The cleavage reaction of S-type and P-type lignin dimmers in the same conditions also gave the degradation product in high yield.

2009-P16

MWL 抽出残渣の分画と分析 — Hemicellulose-Lignin fraction (HCL) のキャラクタリゼーション—

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Fractionation and analysis of wood meal after extraction of MWL —Characterization of Hemicellulose-Lignin fraction (HCL) —

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Abstract: Wood meal after extraction of MWL and the following extraction with LiCl/DMAc was extracted with 3M NaOH solution to get Hemicellulose-Lignin fraction (HCL). HCL was composed of much hemicellulose and lignin in it. But the presence of Lignin-Carbohydrate Complex (LCC) bonds was unclear by the combination method of enzymatic treatment and GPC analysis. Then, HCL was further acetylated and extracted with chloroform to afford Xylan-Lignin fraction (XL). XL had much xylan and lignin, and lignin-xylan bonds strongly suggested by the above combination method. Accordingly, XL may be a useful fraction for the LCC bonds analysis.

2009-P17

リグニンモデル化合物の間接電解酸化反応(2) —mediator の検討—

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Indirect electrooxidation of lignin model compounds (2) —mediated by 1-hydroxybenztriazole, violuric acid and 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonate)—

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Abstract: Indirect electrooxidation of lignin model compound, 1-(4'-ethoxy-3'-methoxy- phenyl)ethanol (1G) using laccase mediators, such as 1-hydroxybenztroazole (HOBT) , violuric acid (VLA), 2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS), was investigated to introduce carbonyl group at a-position. The yields of the corresponding carbonyl compound 2G were about 50 % (HOBT or VLA mediated) and 20% (ABTS mediated). They are useful mediators for the indirect electrooxidation of natural lignin, although yields of 2G by these mediators were lower than that by N-hydroxyphthalimide (NHPI).

2009-P18

木材の酵素糖化におけるイオン液体前処理の効果

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Pretreatment with ionic liquids for enzymatic saccharification of wood

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Abstract: Pretreatment with ionic liquids, 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]) or 1-butyl-3-methylimidazolium acetate ([C4mim][Ac]) was studied for producing glucose from Japanese beech by enzymatic hydrolysis. Beech wood was easily liquefied by [C4mim][Ac] treatment than [C2mim][Cl] treatment. Decrystallization of cellulose in wood was significant by [C4mim][Ac] treatment. Wood components liquefied in ionic liquids were recovered by adding water to the ionic liquids. By enzymatic saccharification with cellulase for these recovered wood components, it was found that ionic liquids pretreatment was effective to enhance glucose productivity. It was also clarified that much glucose yields can be attained by the pretreatment with [C4mim][Ac], compared to that with [C2mim][Cl].

2009-P19

イオン液体中での非フェノール性 β-O-4 型リグニンモデル化合物の反応挙動

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Reaction behaviors of non-phenolic β-O-4 type lignin model compounds in ionic liquids

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Abstract: Reaction behaviors of non-phenolic β-O-4 type lignin model compounds in ionic liquids have been examined. In ionic liquids at 150ºC, guaiacyl type model compounds, erythro (E) and threo (T) form veratrylglycerol-β-guaiacyl ethers (VG), were decomposed slower than corresponding phenolic model compounds, gaiacylglycerol-β-guaiacyl ethers (GG). In the ionic liquid of 1-Butyl-3-methylimidazolium chloride, E-VG was decomposed faster than T-VG. By contrast, significant differences in the decomposition rates were not observed in 1-Ethyl-3-methyl- imidazolium acetate. Syringyl type non-phenolic model compound of T-veratrylglycerol-beta- syringyl ether was decomposed slower than VGs. This result would be related with the difference in the decomposition rate appeared between softwood and hardwood in an ionic liquid.

2009-P20

両親媒性リグニンの調製及びセメント分散剤としての評価

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Preparation of amphiphilic lignin derivatives and evaluation of their viability as cement dispersant

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Abstract: Several polyethylene glycols were introduced to isolated lignins to prepare amphiphilic lignin derivatives. Among them, a lignin derivative with dodecyloxy-polyethylene glycol glycidyl ether (DAEO) showed as high surface activity as a commercially available surfactant. To use those derivatives as cement dispersants, the dispersibility was evaluated. Although LS is actually used as a dispersant of cement, most lignin derivatives showed much better dispersibilities than LS. In addition, the dispersibility of LS was dramatically improved by the reaction with a small amount of DAEO. Thus, this study demonstrated that the amphiphilic lignin derivatives in this study were useful for cement dispersants.

2009-P21

リグニン／PEO ポリマーブレンドの熱流動特性

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Thermal fluidity of the polymer blend of lignin and PEO

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Abstract: Thermal viscous behavior of the blends of alcohol lignin (AL) and PEO were examined using thermo-mechanical analysis (TMA) and capillary viscometer. Both of the initiation temperature of the thermal flow and thermal viscosity of AL was decreased by the blending with PEO. However, by contraries, that temperature and thermal viscosity was increased by the incorporation of excess amount of PEO. Those thermal behaviors are good agreement with the changes in the thermal formability of AL/PEO blend, such as thermal spinning temperature.

2009-P22

バイオディーゼル燃料生産副産物グリセリンと工業リグニン由来原料からのポリウレタン誘導体の調製と物性

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Preparation and properties of polyurethane foams derived from industrial lignins and crude gycerin from BDF industry

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Abstract: Polyurethane (PU) foams were prepared using crude glycerin (CG) obtained as a by-product of the biodiesel fuel (BDF) industry and lignosulfonate (LS) obtained as a by-product of the pulping industry. LS and CG were dissolved in polyethyleneglyco1 (PEG), and two kinds of polyols LSP and CGP were prepared. CG content was varied 0, 5, 10, 15, 20 % in polyols. The above polyols were reacted with poly(phenylene methylene) polyisocyanate (MDI). Water was used as a foaming reagent. Apparent density of PU foams was in a range from 0.09 to 0.07 g cm^{-3}. Compression strength (σ_{10}) was in a range from 0.31 to 0.51 MPa. Scanning electron micrographs of the prepared PU foams were examined.

2009-P23

木質系バイオマス糖化残渣を主成分とする低炭素型プラスチック充填材の製造に関する研究

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Research on the production of plastic filler by utilization of fermentation residue obtained from the wood-derived bio-ethanol production process

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Abstract: In the production procedure of ethanol from woody biomass, about 60-80 wt% of fermentation residue is produced on the base of wood feedstock. We produced the neat biomass- derived synthesized resin complex from the mixed feedstock of the fermentation residue obtained from the wood-derived bio-ethanol production process with glycerol and poly-lactic acid. In the evaluation of the biomass-derived synthesized resin complex as plastic filler, its blending with poly-propylene resin exhibited the better dispersion compatibility and processing performance compared to those produced from the crude saccharification residue. In addition, the melting viscosity of the complex resin was not affected so much by its addition, keeping the stable processing performance, while the addition of the crude residue considerably increased the viscosity.

2009-P24

リグニンからの紫外線吸収剤の開発

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Development of ultraviolet absorbers from lignin

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Abstract: Currently, ultraviolet absorbers are becoming popular due to cosmetic and medical purposes. Exposure of skins to ultraviolet rays from the sun causes damage of the skins. Excessive exposure induces skin cancer and aging. Although the demand for UV absorbers with high safety and minimum environmental impact is becoming increasing, most of the organic UV absorbers currently available are synthetic compounds from petroleum. Therefore, we started the research to develop UV absorbers &om natural aromatic polymer, lignin. By extensive screening of degradation products from lignin, we found the products having high absorbance in UV A and UV B regions.

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2010-101

イネ節間の細胞壁成分合成が異常になる*d50*変異体の解析と*D50*遺伝子の同定

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Histochemical analysis of rice *d50* mutant internodes exhibiting abnormal synthesis of cell wall materials and isolation of *D50* gene

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Abstract: Previously, we reported that parenchyma cells in the elongated internodes of Fukei 71 (*d50* mutant) ectopically deposit grass-specific cell wall material, polysaccharide-linked hydroxy- cinnamoyl esters. Through map-based cloning, we revealed that the *D50* encodes putative inositol polyphosphate 5-phosphatase, which may be involved in phosphoinositide signaling pathways required for many essential cellular functions including cytoskeleton organization, endocytosis and vesicular trafficking in eukaryotes. Further analyses of *d50* phenotype revealed that the *d50* mutation induced abnormally oriented cell division, ectopic deposition of cell wall pectins and thick actin bundles in the parenchyma cells of the intercalary meristem.

2010-102

Sphingobium sp. SYK−6株由来の*ligD*遺伝子を発現する遺伝子組換え植物の作出と解析

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Generation and analysis of transgenic plants with *ligD* gene isolated from *Sphingobium* sp. SYK-6

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Abstract: *Sphingobium* sp. SYK-6 can catabolite various types of phenolic compounds including monolignols, their precursors and lignin dimers. Several genes involved in the catabolism of these compounds have been isolated from this strain in our previous studies. For modification of lignin biosynthesis in plant cell, we focus on l*igD* gene, which encodes Cα dehydrogenase for first step of cleavage of ether bond in compounds with β-O-4 bond. After optimization of codon usage of the gene for efficient expression, we introduced a modified *ligD* gene into tobacco BY-2 cells and *Arabidopsis* plants. Characterization of the transgenic cells and plants will be discussed.

2010-103

高機能性微生物による木質バイオリファイナリー ～Phanerochaete sordida YK−624株におけるリグニン分解性ペルオキシダーゼと5−アミノレブリン酸シンターゼの関係～

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Woody biorefinery with functional microorganisms. — Relationship between ligninolytic peroxidases and

5-aminolevulinic acid synthase in *Phanerochaete sordida* YK-624 —

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Abstract: To overproduce ligninolytic peroxidases (manganese peroxidase (MnP) and novel lignin peroxidase) in *Phanerochaete sordida* YK-624, the gene of 5-aminolevulinic acid synthase (ALAS), *aas*, is involved in the production of 5-aminolevulinic acid which is the rate-limiting step in the biosynthesis of heme, was cloned. The deduced amino acid sequence of *aas* showed highest identity (93.0%) with ALAS from *P. chrysosporium* ME-446. The promoter of glyceraldehyde-3- phosphate dehydrogenase (GPD) gene cloned from *P. sordida* YK-624 was used to drive the expression of *aas*. The expression vector was transformed into a *P. sordida* YK-624 uracil auxotrophic mutant, UV-64. Three transformants showed high MnP activities compared with control transformants into which only *ura5* was introduced.

2010-104

高機能性微生物による木質バイオリファイナリー ～新規リグニン分解特異的プロモーターを用いた超高活性リグニン分解菌の分子育種～

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Woody biorefinery with functional microorganis. Molecular breeding of superior lignin-degrading fungi using novel ligninolytic condition-specific promoter

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Abstract: BUNA2 is one of high produced proteins from hyper lignin-degrading fungus *Phanerochaete sordida* YK-624 under wood-rotting condition. In the transcriptional analysis, the gene of BUNA2 (*bee2*) was stably and strongly transcribed during 20 days cultivation in beach wood meals. A promoter region of *bee2* (*bee2* promoter) was cloned using TAIL PCR and inverse PCR method. The obtained promoter was used to drive the expression of Lip gene (*ylpA*) or MnP gene (*mnp4*), and these plasmids (pBUNA2pro-ylpA and pBUNA2pro-mnp4) were constructed. Protoplasts of UV-64 were mixed with DNA solution containing pBUNA2pro-ylpA, pBUNA2pro- mnp4 and p*PsURA5*, and co-transformed by PEG method. With the same method, DNA solution containing pBUNA2pro-ylpA and p*PsURA5*, and pBUNA2pro-mnp4 and p*PsURA5* were co-transformed respectively. We obtained 17 of *ylpA* & *mnp4*-introducing clones, 9 of *ylpA*- introducing clones, and 14 of *mnp4*-introducing clones.

2010-105

高機能性微生物による木質バイオリファイナリー ～新規糖化酵素産生微生物の探索～

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Woody biorefinery with functional microorganisms —Screening of functional saccharification enzyme-producing microorganisms—

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Abstract: To isolate functional saccharification enzyme-producing bacteria, a decayed wood-pulp perfusion system was developed and applied. An enrichment culture in decayed wood-pulp perfusion system contained at least ten bacteria after two month perfusion and then two strains (E814-1 and E814-2) were isolated as cellulase-producing microorganisms. Among them, strain E814-2 was identified as *Paenibacillus* sp. using 16S rDNA sequencing and this strain closely related to *Paenibacillus curdlanolyticus* which was reported recently as multienzyme complex (cellulosome)- producing bacteria. This result indicates that pulp perfusion system is a useful method for isolate saccharification enzyme-producing bacteria. Additionally, to identify potential enzymes from nonculturable microbes, metagenomic libraries were constructed from several

lignocellulose-rich environments. Around 7.5 kbp eDNAs were successfully cloned and applied to plate assay for screening.

2010-106

リグニン分解酵素による医薬品類の除去

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Elimination of pharmaceutically active compounds by ligninolytic enzymes

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Abstract: Carbamazepine (CBZP) is used as an antiepileptic drug and is highly persistent. In this study, CBZP was treated with manganese peroxidase (MnP), laccase and the laccase-mediator system with 1-hydroxybenzotriazole (HBT). The laccase-HBT system is most effective in eliminating CBZP among the three enzymatic treatments. A single treatment with laccase and HBT eliminated CBZP by about 22% after 24 h, and repeated treatments with laccase and HBT, which were added to the reaction mixture every 8 h, helped eliminate about 60% of CBZP after 48 h. This suggests that repeated treatment is effective in eliminating CBZP. Mass spectrometric analyses demonstrated that two degradation products of CBZP,10,11-dihydro-10,11-epoxycarbamazepine and 9(10H)-acridone, were formed via repeated treatment with laccase and HBT. Furthermore, the anti-inflammatory drug indomethacin (IMC) was also treated with MnP, laccase and the laccase- HBT system. MnP and the laccase-HBT system almost completely eliminated IMC after 4 h of treatment, suggesting that these two enzymatic treatments are effective in eliminating IMC.

2010-107

Bioremediation of DDT by *Pleurotus ostreatus* spent mushroom waste: involvement of ligninolytic enzymes and application in historically contaminated soil

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Abstract: In our previous work, spent mushroom waste (SMW) of *Pleurotus ostreatus* (Hiratake) was shown to have high ability to degrade and mineralize DDT (1,1,1-Trichloro-2,2-bis(4-chloro- phenyl)ethane) in artificially contaminated soil. In present study, SMW of Hiratake was applied to the historically contaminated soil which collected from pesticide manufacturing site in Japan. DDT concentration in the historically contaminated soil is 0.4 mmol/g dry weight of soil. After 28 days incubation, approximately 70% of DDT was degraded compared with autoclave-killed control. Degradation mechanisms especially involvement of ligninolytic enzymes were investigated. SMW of Hiratake has 0.26, 1.90, and 0.13 mmol/min/ml of laccase, MnP, and LiP activities, respectively. High MnP activity suggested MnP seems a key enzyme for degradation of DDT. DDT was treated with purified MnP, and DDD (1,1-dichloro-2,2-bis-(4-chlorophenyl) ethane) and DBP (4,4-dichlorobenzophenone) were detected as metabolic products.

2010-108

白色腐朽菌 *Phlebia* 属菌によるクロルデンの処理

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Biodegradation of chlordane by white rot fungi, *Phlebia* genus

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Abstract: The organochlorine pesticide, chlordane was used as the substrate for degradation experiment with the white rot fungi *Phlebia lindtneri*, *Phlebia brevispora* and *Phlebia aurea*, which are capable of degrading dieldrin, heptachror and heptachlor epoxide. Pure culture of fungi with chlordane (0.25mmol/flask) showed that over 50% of chlordane disappeared in Kirk (LN) medium and PDB medium after 42-day incubation period. Chlordane was biotransformed to heptachlor, heptachlor epoxide, dichlorochlordene, oxychrordane and several hydroxylated metabolites, which have not been reported as bacterial metabolite. 1-aminobenzotrjazole and piperonyl butoxide strongly inhibited the degradation of chlordane and concomitant accumulation of metabolites, indicating cytochrome P450 mediated metabolism.

2010-109
C heavy oil degradation in sea water liquid medium by *Fusarium* sp. F092
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Abstract: Oil contamination have became serious problem in environmental generated via several accident on production. Experiments were carried out to evaluate the ability of *Fusarium* sp. F092 to degrade C heavy oil on sea water liquid medium. The strain F092 grew 0.41 cm/day on potato glucose (PG) agar medium containing C heavy oil. C heavy oil used in our experiment contained 44% of aliphatic, 31% of aromatic, 8% of nitrogen, sulfur and oxygen (NSO) and 17% of asphaltene. At 60 days incubation, degradation of C heavy oil by strain F092 fungus was obtained at the level 77% on those aliphatic and aromatic fractions, and 56 % of total petroleum hydrocarbon (TPH) degradation. The effect of manganese (Mn) addition, could increase 20% of TPH degradation, those are 75% of (NSO) and 31% of asphaltene. The highest activity of manganese peroxidase and laccase reached at 69 UI^{-1} and 49 UI^{-1} on 20 days, while 1,2- and 2,3-dioxygenase showed the highest level after 20 days.

2010-110
Degradation of 2,4,8-Trichlorodibenzofuran by fungi selected from nature
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Abstract: Dioxin can be serious problem for environmental because of its strong toxicity and mutagenicity. White rot fungi are well known for their outstanding ability to produce extracellular oxidative enzymes, which are involved in the degradation of either lignin than a wide range of pollutants include dioxins. Fungus U97 screened from nature had ability to degrade 2,4,8-TCDF by 43%, on 15 days and 61%, on 30 days, respectively. The maximum enzyme activity of strain U97 during 2,4,8-TCDF degradation was 1,2-dioxygenase (262.8 UI-1) and Lip (93.6 UI-1). Carbon source, surfactant and agitation have no negative effect on the growth of U97 during biodegradation of 2,4,8-TCDF on 15 and 30 days. The finding suggest that U97 can metabolize 2,4,8-TCDF to 3,5-dichlorosalicylic acid.

2010-111
白色腐朽菌由来の酵素および酵素製剤を用いたアゾ染料の分解
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Degradation of azo dyes with a crude enzyme and immobilized enzyme from white rot fungi
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Abstract: To purify effluents from textile industry, food industry and so forth, degradation of three kinds of azo dyes, Reactive Red (RR4), Reactive Black 5 (RB5) and Reactive Green 19 (RG19) was conducted by using a crude enzyme and immobilized enzyme from a white rot fungus, PL1. Degradation rate of the dyes by the crude enzyme in liquid medium was about 20 to 87 %. However, the degradation rate was increased to about 90 to 95% by addition of Tween 80. On the contrary, degradation rate of the dyes by the immobilized enzyme (double capsule) in the medium was about 80 to 93%. To conduct the degradation of the dyes using bioreactor packed with the double capsule, effects of flow rate on degradation of the dyes were investigated. It was found that the degradation rate was increased when the flow rate became faster, or the treatment time got longer. The maximum degradation rate of RG19 was 95% when the treatment was conducted for 48 hours at 7.0/min.

2010-112
シロイヌナズナ T87 培養細胞のリグニン分析
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Lignin analyses of *Arabidopsis thaliana* T87 cells

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Abstract: *Arabidopsis thaliana* is the most widely used model plant in the area of plant bioscience sector. T87 is one of the typical lines of *A. thaliana* cultured cells. This cell line has various advantages in the research of plant metabolism, as well as intact *A. thaliana* plants. However, nothing is known about the lignins of T87 cells. In this study, we characterized lignins of T87 cells using six lignin analytical methods, phloroglucino1-hydrochloric acid staining, thioacidolysis, nitrobenzene oxidation, alkaline hydrolysis, and Klason and acetyl bromide methods. These analyses clearly showed that lignins of T87 cells are composed of guaiacyl and *p*-hydroxyphenyl units, and are quite different from lignin found in the *A. thaliana* inflorescence stem, which are composed of guaiacyl and syringyl units.

2010-113

The finding and characterization of hindered LCC by the fractionation of wood cell wall components using LiCl/DMSO system

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Abstract: The fractionation of wood cell wall components was achieved by the application of the LiCl/DMSO solvent system developed in our previous study. Various soluble and insoluble fractions were prepared from beech milled wood by extractions with DMSO containing different amounts of lithium chloride (LiCl) for the study of lignin-carbohydrate complex (LCC). Nitrobenzene oxidation (NO) analyses demonstrated that the lignin in the soluble fractions always has lower yields of NO products consisting of syringaldehyde + syringic acid (S) and vanillin + vanillic acid (V). The syringyl ratios, S/(S+V), were also lower than in insoluble fractions. Accordingly, lignins with lower syringyl ratios are better soluble than those with higher ones. The former is typical in primary wall and the latter in secondary wall. Solubilization of glucan is significantly dependent on the LiCl concentration in DMSO. In the absence of LiCl, only about 6% of glucan was found in the soluble fraction, but about 40% of lignin and xylan were solubilized. The additional 40% of lignin and xylan became soluble together with glucan solubilization by the addition of LiCl up to 3% concentration. However, a fraction amounting to 13% (based on the whole wood) is still remained as a residue under these conditions. Glucan solubilization could not be the reason for this observation as ball-milled cellulose is soluble in 3% LiCl/DMSO. Probably, strong interactions between lignin and carbohydrates prevent solubilization of this fraction, which is denominated here as "hindered LCC", that has never been isolated and analyzed in previous studies. The "hindered LCC" contains non-condensed-type lignin and featured by strong interactions between lignin, hemicelluloses, and cellulose. On the other hand, Björkman LCC, which is obtained when LiCl concentration is O%, is rich in condensed-type lignin and characterized by interactions between lignin and hemicelluloses.

2010-114

Relationships between hemicellulose composition and lignin structure of LCC fractions

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Abstract: New fractionation method of wood cell wall components was applied to selected wood species (beech and red pine). Finely ground wood meal was first extracted by aq dioxane and DMSO to obtain conventional Björkman lignin and LCC. The residue was then subjected to successive extraction by DMSO with increasing content of LiC1 (0.5 to 3.0%). Relationships between lignin structure and carbohydrates in obtained fractions were examined. Syringyl ratio of soluble fractions was always lower than that obtained for corresponding insoluble fractions. It was confirmed that MWL represents very specific part of whole lignin. With the increase of LiCl concentration of the extraction solvent, the lignin content and weight ratio of hemicellulose in sugars decreased, and weight ratio of cellulose in sugars increased.

2010-115

高CO_2下で生育した樹木の細胞壁構成成分の評価

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Evaluation of wood cell wall component growing under elevated CO_2

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Abstract: Chemical characterization of the wood which was grown under free air CO_2 enrichment (FACE) was investigated. We focused on lignin to detect the effect of increasing atmospheric concentration of CO_2 to wood material. We characterized lignin using the acetylbromide method for lignin content and the thioacidolysis to examine the syringyl/guaiacyl (S/G) monomer ratios. The results show no significant difference between FACE and control samples, which indicates elevated CO_2 environment would not induce the change of lignin content, S/G monomer ratios.

2010-116

木質バイオマスリファイナリーのための高分解能質量分析法の開発

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Development of high-resolution mass spectrometry for woody biomass refinery

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Abstract: Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI- TOF MS) gives direct structural information in a wide range of molecular mass regions. However, reports on the structural analysis of lignin by MALDI-TOF MS are still limited. In this study, milled wood lignin (MWL) from Japanese ceder, *Fagus crenata* and *Eucalyptus globulus* wood were analyzed MALDI-TOF MS. The mass spectrometry provided peaks of the lignin including those characteristic to β–*O*-4 linkage, a major linkage among monomeric units in lignin. The mass spectrometry is useful for woody biomass refinery, especially for structure-based utilization of lignin.

2010-117

HSQC NMR analysis of bamboo lignin and bamboo cell walls

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Abstract: In situ acetylated mature and immature hachiku bamboo (*Phyllostachys nigra* Munro *var. Henonis*) cell walls were characterized by ^1H-^{13}C correlation heteronuclear single quantum coherence (HSQC) NMR spectroscopy. The lignins from mature and immature bamboo were also isolated in order to assign the lignin fraction. The HSQC spectrum of immature bamboo lignin and plant cell walls can help studying the lignification of bamboo.

2010-特別講演

リグニン利用の現状と将来展望

西盛嘉人
日本製紙ケミカル株式会社開発研究所

The current industrial applications of the lignin and its prospect

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Abstract: Commercial lignin is produced as a co-product of the pulp industry. Lignins are products of Kraft and Sulfite pulping process. The Kraft lignin is mainly used as a fuel through a recovery boiler. On the other hand, the lignosulfonate generated from the Sulfite pulping process is used as a concrete admixture, binder and for other applications due to its dispersing, binding, complexing and emulsifying properties. This presentation will introduce the current industrial applications of the lignin. Furthermore, new possible applications such as a raw material for bio-refineries are discussed as well.

2010-201

リグニンモデル化合物の間接電解酸化反応（3）—β-O-4 モデルオリゴマーの NHPI 間接電解—

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Indirect electrooxidation of lignin model compounds (3) — NHPI-mediated indirect electrooxidation of β-O-4 model oligomers —

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Abstract: Indirect electrooxidation of β-O-4 type oligomeric lignin model compound using N-hydroxyphthalimide PHPI) as an mediator was studied to introduce carbonyl group at α-position. It was suggested from the NMR data of the electrolysis products that carbonyl group was introduced to α-position of the oligomer in 68-84% yield. These results suggest that NHPI-mediated indirect electrooxidation is an effective method for α-carbonylation of natural lignin structures.

2010-202

イオン液体中でのリグニンモデルおよびリグニンの構造変化

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Structure changes of lignin model compounds and lignin preparations in ionic liquids

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Abstract: To examine the structure changes of lignin in ionic liquids (IL), MWL was treated with IL under the heat conditions. After IL treatments, some portions of MWL were recovered as water soluble fractions. In FT-IR analysis, the band assigned to conjugated carbonyl groups, which was clearly detected for original MWL, were dramatically decreased by the IL treatment. ^{1}H-NMR estimated the differences in the side-chain structures between the water insoluble fractions and original MWL. In this presentation, we will discuss the structure changes of lignin preparations in ILs by comparing them with those of lignin model compounds.

2010-203

活性酸素種との反応における非フェノール性リグニンモデル化合物のベラトリル芳香環と側鎖水酸基の位置の影響について

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Effect of veratryl aromatic ring and location of side chain hydroxyl group on the reaction of non-phenolic lignin model compounds with active oxygen species

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Abstract: Each of a non-phenolic β-O-4 type dimeric lignin model compound, 2-(3,5-difluoro-phenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (VDF), or a β-O-4 type model compound,
2-(3,5-difluorophenoxy)propane-1,3-diol or 3-(3,5-difluorophenoxy)propane-1,2-diol, was subjected to an oxygen alkaline treatment in the presence or absence of a generator of active oxygen species (AOS), 4-hydroxy-3-methoxybenzyl alcohol (VA). AOS are generated by the reaction of VA with oxygen. The incorporation of 3,5-difluorophenoxyl group in the structure of the model compounds is to detect 3,5-difluorophenol (DFPh) when DFPh is liberated from the model compound during the treatment. It was suggested that AOS attack the side chain of VDF and non-phenolic 3,5-difluoro- phenoxyl group in VDF is

converted to DFPh, a phenolic compound. The effect of existences of veratryl aromatic ring, benzyl hydroxyl group, and secondary hydroxyl group on the reaction of the model compounds with AOS is also discussed.

2010-204

過酸化水素−アルカリ処理におけるシリンギルおよびグアイアシルリグニンモデル化合物の分解の比較

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Comparison of the degradation of syringyl and guaiacyl type lignin model compounds in alkaline hydrogen peroxide treatment

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Abstract: Non-phenolic lignin model compounds, 1-(3,4-dimethoxyphenyl)ethane-1,2-diol (G), 1-(3,4,5-trimethoxypheny1)ethane-1,2-diol (S),1,2-dimethoxybenzene (G'), and 1,2,3-trimethoxy- benzene (S'), were reacted with hydroxyl (HO•) and oxyl anion (O•–) radicals, which were generated by the decomposition of hydrogen peroxide under alkaline conditions bH 12.0, 70Qc). The degradation of G was not very different from that of S, which suggests that the difference in the aromatic structure does not have significant influence on the reaction. The degradation of G' was clearly greater than that of S' but much smaller than those of G and S. These results suggest that the side chains of G and S are predominantly attacked by O•– (and HO•) and that high electron density of aromatic ring interferes with the reaction with O•– (and HO•).

2010-205

半流通型２段階加圧熱水処理によるブナ由来水可溶性リグニンの分析

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Characterization of water-soluble lignin-derived products from Japanese beech as treated by semi-flow two-step hot-compressed water

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Abstract: Japanese beech was treated by two-step semi-flow hot-compressed water (1st stage: 230ºC/10MPa/15min, 2nd stage: 270ºC/10MPa/15min). Interestingly, 34.4% of lignin was recovered in the water-soluble portion at the 1st stage. In order to characterize lignin-derived products, the water-soluble portion at the 1st stage was extracted with ethyl acetate, and ethyl acetate layer and water layer were separated. UV absorption which is characteristic of aromatic ring was detected in both the water layer and the ethyl acetate layer. Some mono-saccharides were detected from the ethyl acetate layer after hydrolysis. These results may be suggested that some lignin-derived products at the lst stage were related with saccharides from hemicelluloses, it is likely lignin- carbohydrate complex (LCC).

2010-206

リグニン熱分解中間体としてのカテコール、ピロガロール、クレゾール、キシレノール類の熱分解反応

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Pyrolysis reactions of catechols, pyrogallols, cresolS and xylenols as lignin pyrolySis intermediates

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Abstract: Secondary reactions of lignin pyrolysis intermediates were studied with a closed ampoule reactor under N_2 at 600ºC for 40-600 s. Two types of the intermediates were used; catechols and pyrogallols as products of O-CH_3 homolysis pathway; cresols and xylenols as those of OCH_3 rearrangement pathway. As a result, it was found that additional OH and CH_3 (especially OH) on phenol increase the reactivity, although phenol was fairly stable under the present conditions. Accordingly, O-CH_3 homolysis products especially syringyl-characteristic pyrogallols were more effectively converted into the gaseous products, mainly CO, even at short heating time as 120 s. On the other hand, the OCH_3 rearrangement products were comparatively stable and formed CH_4 and H_2 with coke at longer heating time as 600 s. Selective demethylation at the *o*- and *p*-position to phenolic OH was also observed in cresols, xylenols and trimethylphenol. A two step mechanism was proposed for this demethylation, which include radical coupling of H and C-centered radicals (*o*- or *p*-position) formed from the phenoxy radical intermediates and the following C-CH_3 homolysis. This is confirmed with the calculated BDEs (-60 kcal/mol) of the C-CH_3 bonds in the coupling products. Based on these results of intermediates pyrolysis, pyrolysis reactions of guaiacol and syringol are discussed.

2010-207

アルカリ処理クラフトリグニンのアルミニウムとの錯体形成能およびその毒性除去能に対するフェノール性水酸基の寄与に関する研究

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Studies on contribution of phenolic hydroxyl groups in kraft lignin to complexation with aluminum and reducing its toxicity

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Abstract: Contribution of phenolic hydroxyl groups, including catechol type structures, in alkaline-treated kraft lignin to forming complex with aluminum and reducing its toxicity was examined in this study. The soda-cooked lignin, which was shown to be effective in reducing aluminum toxicity and forming aluminum complex, was also used. The results obtained in this study indicate that contribution of catechol structures in alkaline-treated kraft lignin and soda-cooked lignin to forming complex with aluminum was insignificant. Phenolic hydroxyl groups in alkaline-treated kraft lignin may contribute indirectly to forming complex with aluminum and reducing its toxicity by increasing its water solubility.

2010-208

Effect of residual lignin in alkali pulps on enzymatic hydrolysis of cellulose

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Abstract: Alkaline sulfite-anthraquinone (AS-AQ) cooking was applied to the pretreatment for enzymatic hydrolysis of cellulose of Japanese larch (*Larix leptolepis*) heartwood. We changed the ratio of Na_2SO_3 in the cooking liquors, and found that the 40% ratio of Na_2SO_3 at chips cooking had the capability of acquiring a high pulp yield and the lowest lignin content compared to others. During the hydrolysis of AS-AQ pulps, the content of glucose hydrolyzed in the enzymatic hydrolysate of a pulp containing a small amount of lignin was higher than that of a pulp containing a large amount of lignin at any cellulase charges (Filter paper cellulase unit: FPU). We determined the enzyme adsorption to the pulps by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS).

2010-209

セルロースの芳香族ヒドロキシ酸エステルにおける熱的特性と液晶性

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Thermal and liquid crystalline properties of cellulosic aromatic hydroxyl acid esters

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Abstract: Liquid crystalline properties of esterification products of cellulose and gallic acid were investigated. Cellulose gallate formed liquid crystalline mesophase on heating between 220 and 230ºC. As a gallic acid molecule possesses three hydroxyl and one carboxyl groups, polycondensed gallic acids as side chain of cellulose can form hyperbranched structure. The thermotropic liquid crystallinity of cellulose gallate is attributed to the hyperbranching nature of poly(gallate) side chains that can interrupt the interaction between cellulosic backbones.

2010-210

リグノスルホン酸／ポリビニルアルコール複合ゲルの調製とキャラクタリゼーション

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Preparation and characterization of lignosulfonic acid/poly (vinyl alcohol) composite hydrogel
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Abstract: Previously, we have prepared lignosulfonic acid (LSA)/poly(vinyl alcohol) (PVA) composite hydrogels via cross-linking with glutaraldehyde (GA) in aqueous solution. In the present study, to avoid elution of the LSA component in aqueous media and increase the LSA content, LSA/PVA composite hydrogels were prepared via blend films cast from their mixed aqueous solutions. Cross-linking moiety was introduced into the blend films by thermal treatment and/or reaction with GA. The retentivity of LSA in aqueous media was improved by formations of hydrogen bonding and sulfonate ester between LSA and PVA, both of which were corroborated by FT-IR measurement. The salt-splitting capacity and activity of the sulfo groups of LSA for the composite gel samples were found to reach ~0.7 mmol/g-gel and ~47 %, respectively.

2010-211
リグニンのエポキシ成形材料への応用検討
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Possible application of lignin derivatives to molding compounds
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Abstract: A more sustainable society by promoting global production that reduces the environmental burden of a product throughout its life cycle is required. We are currently researching the use of woody biomass, particularly the application of woody lignin to the epoxy resin widely used in modern electric and electronic equipment. We have investigated the use of lignin derivatives as molding materials. Melt viscosities of molding compounds containing lignin derivatives as hardening agents were higher than that of a commercially-available molding compound. However, other mechanical and electrical properties of hardened compounds were comparable to those of the hardened commercially-available molding compound. We have successfully applied the molding compound containing lignin to mold a stator of a prototype of motor. Results suggest that woody lignin has great potential for application to electric devices.

2010-212
アシル化リグニンを原料とするエポキシ樹脂の合成と熱的性質
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Synthesis and thermal properties of epoxy resins derived from acetylated alcoholysis lignin
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Abstract: Acetylated alcoholysis lignin (AcAL) was allowed to react with bisphenol A diglycidyl ether (BPADGE) in the presence of a catalytic amount of phosphorous compound. The molar ratio of epoxy groups to acetoxyl groups ([EPOXY]/[PhOAc] ratios, mol/mol) was varied from 0.9 to 1.2. The chemical structure of the obtained epoxy resins was detemined by FT-infrared spectra of epoxy resins. Thermal properties of epoxy resins were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG). Glass transition temperatures (*T*g's) of epoxy resins showed a maximum value at 1.1 of [EPOXY]/[PhOAc] ratio. The activation energy (*E*) of curing reaction was determined by the integral method using values of reaction heats which were obtained by heating samples at various heating rates. The obtained value of *E* was ca. 90-210 kJ/mol. Thermal decomposition temperatures (*T*d's) of epoxy resins were almost constant regardless of [EPOXY]/[PhOAc] ratios, while the residue at 500 ºC (MR_{500}) Of epoxy resins showed a maximum value at of 1.0 of [EPOXY]/[PhOAc] ratio.

2010-213
両親媒性リグニン誘導体の利活用

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Utilization of amphiphilic lignin derivatives

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Abstract: Three types of polyethylene glycol (PEG) derivatives with epoxy group, PEGDE, EPEG and DAEO, were reacted with several isolated lignins to prepare amphiphilic lignin derivatives. The relationships between surface activities of the lignin derivatives and dispersibility or efficiency of cellulase activity enhancement were investigated to make use of the lignin derivatives as cement dispersants and cellulase-aid agents, DAEO-Lignin showed the highest surface activity, followed by EPEG-Lignin and PEGDE-Lignin. These lignin derivatives improved the enzymatic saccharification yield of unbleached pulp. This effect of lignin derivatives is closely related to their surface activities. On the other hand, EPEG lignin had the highest dispersibility. This effect of cement dispersibility did not simply obey the surface activity.

2010-P01

高機能性微生物による木質バイオリファイナリー　～高活性リグニン分解菌 *Phanerochaete sordida* YK-624 株のリグニン分解時に産生されるタンパク質のプロテオーム解析～

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Woody biorefinery with functional microorganisms — Proteomic analysis of proteins produced by hyper lignin-degrading fungus *Phanerochaete sordida* YK-624 under the ligninolytic condition—

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Abstract: Proteomic analyses of proteins produced by hyper lignin-degrading fungus *Phanerochaete sordida* YK-624 under differential ligninolytic condition were carried out. In the fungal-treated unbleached hardwood kraft pulp (under low lignin content condition), some ligninolytic enzymes were mainly detected. On the other hand, catalase, glutathione S-transferase, 1,4-benzo- quinone reductase, enolase, mannose-6-phosphatase, and D-xylose reductase, including ligninolytic enzymes, were detected in the fungal-treated beech wood meals (under high lignin content condition). These results suggest that secreted proteins were different by lignin content of the culture, and that multiple metabolic pathways were activated under high lignin content condition.

2010-P02

高機能性微生物による木質バイオリファイナリー

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Woody biorefinery with functional microorganisms

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Abstract: Biorefinery process is environmental friendly and low-energy cost technology. Ethanol can be also biorefined from lignocellulosic material. There are two big problems on the biorefinery of woody materials for ethanol fermentable sugar. First is low-efficiency of biological treatment for lignin removal. Second, enzymatic saccharification process is less efficiency and its cost is quite expensive comparing with chemical process. Our final goal is the establishment of biorefinary process that can obtain fermentable sugars from woody material, especially from cedar wood. We are constructing functional organism that is capable to effective lignin-removal from wood, and screening of environmental microorganisms that produce functional glycosidases.

2010-P03

パラコツカス属細菌によるリグニンの分解

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Biodegradation of lignin by *Paracoccus* sp.

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Abstract: In this study, DHPs were subjected to the degradation by *Paracoccus*. sp. and the degradation products were investigated. After the degradation, the molecular weight of DHP was decreased and some phenolic compounds, such as salicylic acid, 2,3-dihydroxybenzoic acid, vanillin and vanillic acid were produced. When the ^{13}C-[α]-labeled DHP was degraded, ^{13}C-[α]-labeled vanillin and vanillic acid were yielded. Salicylic acid and 2,3-dihydroxybenzoic acid were also produced, however they were not labeled. These four compounds were not yielded when the culture was occurred with glycerin as a sole carbon source. Thus it can be concluded that salicylic acid and 2,3-dihydroxybenzoic acid were also produced from DHP.

2010-P04

カワラタケの産生する天然型ラッカーゼメディエータ

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Natural laccase mediator from the culture fluid of *Trametes versicolor*

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Abstract: To elucidate the presence of natural laccase mediator, we searched for components in the culture fluid of laccase-producing medium of *Trametes versicolor*. Anthracene, which is not oxidized by laccase alone, was used for the assay of the ability of laccase mediator. An active fraction was obtained from the ethyl acetate extracts by repeated chromatography, ant it was analyzed by GC-MS. It is revealed that *p*-hydroxybenzoic acid (HBA) was contained in the fraction. Then, to clarify the mediator ability of HBA, the oxidations of anthracene, reactive black 5 and nonphenolic β–*O*-4 lignin substructure model compound by laccase-HBA couple were conducted. The results demonstrated that all substrates were extensively decreased by this treatment.

2010-P05

アイソザイム分析及び NALDI-TOF-MS 分析によるカバノアナタケ菌 IO−U1 株に感染したシラカンパ No. 8 幼植物体の防御応答の解明

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Clarifying defence responses in Japanese birch No.8 plantlets infected with *Inonotus obliquus* IO-U1 strain by analyses of peroxidase isozyme and NALDI-TOF-MS

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Abstract: It has been found that lignin and phenolic compounds accumulate, and peroxidase activity appears in Japanese birch plantlets immediately after the infection with *Inonotus obliquus*. In this study, invasion of the fungal hypha into tissues of the plantlets was observed by a scanning electron microscope. After 10 and 30 days of infection, invasion of the fungal hypha into vessels and wood fibers were observed in the plantlets. These results suggest that lignin and phenolic compounds were accumulated to protect the plantlets from invasion of the fungal hypha. Analyses of peroxidase isozyme and Nano-Assisted Laser Desorption / Ionization (NALDI) –TOF-MS are currently under way.

2010-P06

ポプラ引張あて材細胞壁の木化過程

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Lignification process of lignified cell wall layers in poplar tension wood

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Abstract: Lignification process of delignified cell wall layers namely, S1, S2 and compound middle lamella in poplar tension wood fibers was examined by UV microscopy and TEM. Formation process of G layer was compared to clarify that these lignified cell wall layers finish lignification before G layers are deposited or that lignification of these layers progresses during G layer formation. As a result, the UV absorption and also contrast in potassium permanganate staining in TEM in these lignified cell wall layers increased during G layer formation. This result suggests that lignification of these layers progresses during G layer formation.

2010-P07

MWL 抽出残渣の分画と分析（II） — Xylan-Lignin fraction (XL) のキャラクタリゼーション —

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Fractionation and analysis of wood meal after extraction of MWL（II） —Characterization of Xylan-Lignin fraction (XL)—

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Abstract: Xylan-lignin fraction (XL), which was prepared by several fractionation steps from wood meal after extraction of MWL, was characterized by conventional analytical methods. XL was found to be mainly composed by syringyl lignin with β–O-4 structure and xylan. Furthermore, XL was fractionated with dioxane/water (9:1) to give a soluble fraction (named DL) and a insoluble fraction (DLR). The former and the latter are mainly composed by syringyl lignin with β–O-4 structure and xylan, respectively. DLR is one of promising fractions for elucidation of LCC-bonds.

2010-P08

ケイ素吸収欠乏イネ突然変異体 lsi1 におけるリグニン分析

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Analysis of the lignin in a silicon uptake-deficient mutant *lsi1* of rice

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Abstract: A rice mutant *lsi1* accumulates less silicon in the shoots than a wild type rice (cv. Oochikara). The mutant *lsi1* and the wild type were planted in seedling cases, lignin contents in leaf and stem tissues were determined with Klason method. Lignin contents in leaves and stems of *lsi1* were higher than those of the wild type. Lignin contents in leaves and stems of *lsi1* planted in silicon addition soil (Si+) were lower than those in control soil (Si-). While cellulose contents in leaves and stems of *lsi1* were slightly higher than those of the wild type. These results suggested that silicon accumulation in rice might have a negative influence on the deposition of lignin and cellulose, and formation of the secondary cell walls, and thus it affected mechanical strength of rice.

2010-P09

DFRC 法による針葉樹の葉リグニンの検出

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Detection of leaf lignin in Japanese gymnosperms by DFRC analysis

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Abstract: A small amount of guaiacyl lignin was detected in sugi leaf by DFRC analysis in our previous report. In this study, the analysis was subjected to major Japanese gymnospermous leaves, hinoki, pine and ginkgo. Pine needle gave relatively much lignin degradates, in contrast, hinoki and ginkgo leaves gave only trace amount. Therefore, there is no lignin with arylether interunit linkages in hinoki and ginkgo leaves. This result shows the obvious difference in leaf-lignin distribution in gymnospermous species. The existence of well-developed cambial tissues is anticipated for the depositing site of lignin in rigid leaf, and pine and sugi leaves seem to have these characteristics.

2010-P10

ハンゲショウにおける 9,9’-デオキシネオリグナン・リグナンの生合成の検討

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Investigation of biosynthesis of 9,9'-deoxy-neolignans/lignans by *Saururus chinensis*

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Abstract: 9,9'-Deoxy-lignans/neolignans have been isolated from mainly Myristicaceae, Lauraceae, and Piperaceae plants. However, their biosynthesis is unknown. The present report describes stereochemistry and biosynthesis of D$^{7'}$-4,7-dihydroxy-3,3'-dimethoxy-8-*O*-4'- neolignane, whose *erythro* and *threo* isomers are named as Machilin C and D, respectively, in *Saururus chinensis* (Saururaceae). (1) The neolignans were prepared by dehydrogenative polymerization of isoeugenol with horseradish peroxidase and H_2O_2. The diastereomeric ratio was *erythro* : *threo* =16 : 84. (2) The neolignans were isolated from the underground parts of *S. chinensis*. The diastereomeric ratio was 0 : 100 and the enantiomeric ratio was (+) : (-) = 2 : 98. To determine the enantiomeric ratio of the preferred diastereomer (Machilin D), its terminal double bond was saturated by catalytic reduction with palladium carbon and chiral HPLC of the resulting dihydro- Machilih D was done. (3) Dehydrogenative polymerization of isoeugenol with a cell-free extract from *S. chinensis* in the presence of H_2O_2 gave the neolignans in the diastereomeric ratio of 14 : 86. However, this Machilin D was racemate. Furthermore, Sauchinon, a 9,9'-deoxy-lignan whose benzene ring lost its aromaticity was isolated from *S. chinensis*. A proposed biosynthetic pathway Sauchinon will be discussed.

2010-P11

β-1 型リグニン二量体モデル化合物の簡便な合成法

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Efficient short step synthesis of β-1 lignin model compound

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Abstract: Efficient short step synthesis of 1,2-Bis(4-hydroxy-3-methoxyphenyl)-1,3-propanediol [β-1 lignin model compound] has been achieved. The key step in the synthesis is hydroboration of 2,3-bis-(4-acetoxy-3-methoxyphenyl) acrylic acid obtained from perkin reaction of vanillin and homovanillic acid. In this strategy, only *threo* forms of desired compound is produced. The efficient conversion process of *threo* form into *erythro* form has also been discussed.

2010-P12

ジリグノールの酵素的脱水素重合

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Enzymatic dehydrogenative polymerization of dilignols

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Abstract: To analyze the reaction kinetics of the dilignols in lignin biosynthesis, we tried enzymatic dehydrogenative polymerization of pinoresinol as a typical dilignol. LC/MS/MS analysis indicated that there were pinoresinol dimers in the reaction mixture. This results suggested that there was a possibility of the polymerization between dilignols each other in vivo. Reaction kinetics of coniferyl alcohol was compared with that of pinoresinol.

2010-P13

tert-ブトキシドによるβ-O-4 結合開裂反応における溶媒の影響

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Effects of the solvents on the reaction of the β-O-4 bond cleavage using *tert*-butoxide

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Abstract: The *β*-O-4 bond cleavage of a dimeric non-phenolic lignin model compound, 2-(2-methoyphenoxy)-1-(3,4-dimethoxyphenyl)ethanol (2), was examined in systems using potassium *tert*-butoxide (KO^{t}Bu)/THF and KO^{t}Bu/1,4-dioxane. The *β*-O-4 bond of (2) was cleaved in both systems at 30ºC and the rates were much greater than those in KO^{t}Bu/^{t}BuOH and KO^{t}Bu/DMSO systems, which had been reported in our previous paper. A characteristic reaction product 1,2-dimethoxybenzene (6), was detected in both systems. (6) was probably produced from 4-acetyl-1,2-dimethoxybenzene (4), a primary degradation product of the *β*-O-4 bond cleavage of (2).

2010-P14

Absolute configurations of erythro- and threo-syringylglycerol-8-*O*-4'-(sinapyl alcohol) ethers, dilignols as well as 8-*O*-4' neolignans

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Abstract: To clarify the stereochemical mechanism of the optically active syringylglycerol-8-*O*-4'-(sinapyl alcohol) ethers (SGSE) formation by the incubation of sinapyl alcohol (SA) with enzyme preparations of *Eucommia ulmoides*, absolute configuration of four stereoisomers, (+)-*erythro*-, (-)-*erythro*, (+)-*threo*-, and (-)-*threo* isomers, of SGSEs that contain a chiral secondary benzyl alcohol were determined as (*7R, 8S*), (*7S, 8R*), (*7S, 8S*) and (*7R, 8R*),respectively, by Mosher's method [^{1}H NMR analysis of tri-(*R*)-(+)-a-methoxy-a-trifluoromethylphenylacetate (MTPA) esters of SGSEs] with our related empirical rules. Four stereoisomers of SGSEs were obtained by dehydrogenations of SA with $FeCl_3$ followed by reversed phase HPLC and chiral HPLC.

2010-P15

ヨウ化アルミニウム処理によるクラフトリグニンの構造変化

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Structural changes in kraft lignin by aluminium iodide (III) treatment

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Abstract: We have been trying to develop a new method to modify technical lignin chemically, aiming at fabricating a novel biomass-based polymer with functionality in terms of biorefinery. In this study, kraft lignin, an important technical lignin, was subjected to a treatment with AlI_3, an effective ether-cleaving reagent under a mild reaction condition, to give lower mass compounds with higher hydroxyl content. As in the case of a lignin polymer model compound in a separate experiment, the AlI_3 reagent was found to degrade KL and increase hydroxyl group significantly, depending on the reaction condition.

2010-P16

フェルラ酸・グリコール酸共重合体の合成および特性解析

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Synthesis and characterization of poly(ferulic acid-*co*-glicolic acid)

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Abstract: Copolymerization of ferulic and glicolic acids were performed to obtain heat-resistant liquid crystal polyester. It was revealed that poly(ferulic acid-*co*-glicolic acid) obtained after a reflux in acetic anhydride/sodium acetate at 160ºC for 18 h formed liquid crystalline mesophase between 162 and 213ºC, in spite of its low molecular weight comprising three ferulic and two glycol units.

2010-P17

カフェ酸をモノマーとする多分岐型ポリエステルの合成及び構造解析

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Synthesis and structural analysis of poly(caffeic acid)

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Abstract: Caffeic acid, a cinnamic acid derivative provided from lignin, can be polymerized to form multi-branched polyester, because caffeic acid has two phenolic hydroxyl groups and one carboxyl group. In this study, synthesis and characterization of poly(caffeic acid) (PCA) were performed. The polymerization was performed in a two-step process. First, caffeic acid was acetylated using acetic anhydride and sodium acetate under a reflux in 160 ºC. Then a polycondensation was performed at 160 ºC under a vacuum. The product was analyzed by using FT-IR, NMR, GPC, MALDI-TOF-MS, DSC and hot stage-equipped polarizing microscope. It was revealed that PCA obtained after polycondensation has a melting point at about 180 ºC and forms anisotropic phase under molten state in response to external mechanical field.

2010-P18

4 級アミン型リグノフェノールによる貴金属の回収

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Recovery of precious metals using quaternary amine type lignophenol

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Abstract: Quaternary amine type derivative of lignophenol (TMA-CLP) was prepared by electron beam irradiation followed by chemical treatment with trimethylamine. The adsorbent was tested for its adsorption behavior for a number of metal ions and found to exhibit selectivity for Au(III), Pd(II), and Pt(IV) in 0.5 to 5.0 M hydrochloric acid medium. From the adsorption isotherm study, the maximum loading capacity of TMA-CLP for Au(III), Pd(II), and Pt(IV) was evaluated as 4.3, 0.74, and 1.3 mol/kg of the dry adsorbent, respectively.

2010-P19

電子ビームによる高機能性リグノフェノール吸着剤の開発

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Development of high functional lignophenol sorbent using electron beam

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Abstract: Wood derived lignin has been modified with ethylenediamine after electron beam irradiation. Its performance for the recovery of precious metals has been studied and the results are compared with that of chemically modified derivative. Electron beam induced modification yielded better performing sorbent. Electron beam is a good tool for synthesis of high functional bio-sorbent.

2010-P20

糖化残渣からのリグニン抽出とその性状評価

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Extract of lignin from saccharification residue and estimation of chemical nature of the lignin

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Abstract: One of the important issues in bio-ethanol production from woody biomass is the effective usage of saccharification residue. The saccharification residue includes lignin, which is contained a variety of functional groups. It is possible to apply the lignin as raw martial for chemical agents and plastics, thus there is a need for an effective extraction technique of lignin from the saccharification residue. In this study, saccharification residue was applied to the extraction technique that was reported in previous study. This report explained that the lignin was extracted from saccharification residue.

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2011-101

β-1 型スピロジエノン構造に関する研究：シリンギル型同モデル化合物と広葉樹リグニンの NMR 化学シフト値の比較

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Study on spirodienone structures with β-1 linkage: NMR chemical shifts of the syringyl type model and the corresponding signals on the HSQC spectrum of hardwood lignin

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Abstract: A novel lignin model compound of syringyl type spirodienone structures (β-1/α-O-α′) was obtained by oxidative coupling of sinapyl alcohol γ-acetate with 1-(4-hydroxy-3,5-dimethoxyphenyl) ethanol. The ^{1}H and ^{13}C NMR chemical shifts of the acetylated model compound were compared with the signals on the HSQC spectrum of acetylated avicenia lignin (MWL). The ^{1}H and ^{13}C chemical shifts of signals from α, β, and γ-positions in one side chain part of the model were in well agreement with the candidate correlation signals of spirodienone structures on the HSQC spectrum of the acetylated MWL.

2011-102

Dissolution of ball-milled plant cell walls in ionic liquid systems for HSQC NMR analysis

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Abstract: Several ionic liquids with and without co-solvent were used to find milder conditions than those reported so far for complete dissolution of ball-milled plant cell walls in ionic liquids. Among the ionic liquids tested, 1-ally-3-methylimidazolium chloride ([Amim]Cl) was the most effective ionic liquid for our purposes. Some co-solvents such as N,N-dimethyacetamide (DMAc) and pyridine were found to be quite effective to increase the solubility of the cell walls. The milled fir wood prepared by ball-milling for 8 h was dissolved completely in [Amim]Cl–DMAc (2:1, w/w) and [Amim]Cl–pyridine (1:1, w/w) even at room temperature (30ºC). 1H–13C correlation HSQC NMR experiments were successfully conducted with the *in situ* acetylated fir wood. The differences between the two solvent systems were discussed based on the spectra.

2011-103

木質バイオマスの定量・微細構造解析のための HSQC/HMBC NMR 法の開発

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Developments for quantitative and microstructural analyses of woody biomass using HSQC/HMBC NMR

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Abstract: Woody biomass is a heterogeneous material and its microstructure is not yet fully understood. Here, we developed an analytical method of intact and biodegraded wood using solution state NMR without any chemical treatment. Wood pieces were milled in mild conditions and dissolved in DMSO-d_6. Optimization of analytical parameters gave high resolution and quantitative HSQC spectra. NMR signals of lignin microstructures were well distinguished and assigned by HMBC correlations. We applied this method to biodegraded wood by white rot fungus and demonstrate a decrease of lignin contents.

2011-104

バイオリファイナリーのためのリグニンの MALDI-FT-ICR MS

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MALDI-FT-ICR MS of lignin for biorefinery

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Abstract: Mass spectrometry by MALDI ionization gives direct structural information in a wide range of molecular mass regions. However, reports on mass spectrometry of lignin by MALDI ionization are still limited. Our group has analyzed isolated and synthetic lignin using MALDI-MS. In this study, the milled wood from *Eucalyptus globulus* was analyzed with ultra-high resolution mass spectrometry with Fourier-transform ion cyclotron resonance mass spectrometer (FT-ICR MS). The mass spectrometry provided the peaks originating from the inter linkages of lignin and hexoses. The mass spectrometry is useful for wood biomass refinery, especially for structure-based utilization of lignin.

2011-105

ToF-SIMS を用いたリグニン構造の解析

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Analysis of lignin structure using ToF-SIMS

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Abstract: From the experiments using model compounds, when lignin is analyzed by ToF-SIMS, the common interunit linkages without 5-5'linkage are cleaved and the characteristic secondary ions of lignin are generated. In previous study, the characteristic secondary ions at m/z 137 and 151 are produced from the phenylcoumaran type lignin model compound by ToF-SIMS. But it is still not clear which aromatic ring generates these ions and whether the β-5' linkage is cleaved by ToF-SIMS. In this study, the phenylcoumaran type lignin model compound and its deuterium-labelled compound were synthesized and analyzed by ToF-SIMS. From the result, the β-5' linkage seems not to be cleaved by ToF-SIMS.

2011-106

IR-SNOM による木質組織の分析

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IR-SNOM analysis of wood tissue

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Abstract: IR-SNOM (Infrared-Scanning near-field optical microspectrometer) is potentially capable of obtaining IR spectra from a microscopic area of submicron order. After the wood fiber of *Quercus serrata* was manually isolated, it was put on the KBr tablet and subjected to IR-SNOM analysis. We succeeded in obtaining a good near-field IR spectrum by omitting the scattering light derived from surrounding tissue. The absorbance peak at around 835cm^{-1} in near-field IR spectrum from wood fiber was stronger than the corresponding peak in the usual IR spectrum obtained from wood powder. Considering that the spectrum obtained from wood powder by usual FT-IR reflects the average spectrum of whole sample, peaks characteristic in near-field IR spectrum may indicate the specific feature of the observed sample.

2011-107

木材の熱分解生成物の定量的検討 ～過ヨウ素酸処理木粉の熱分解生成物とリグニン含有率の関係～

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Quantitative analysis of pyrolysis products of Wood material -Relation with pyrolysates of periodate treated wood material and Lignin contents-

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Abstract: In order to understand the effect of lignin on the formation of pyrolysis products, wood meals

with increased lignin content prepared by periodate pre-treatment were subjectd to pyrolysis by the us of tube type kiln. Lignin content of prepared samples were 45.1% (by 4days periodate treatment) and 67.6% (by 7days periodate treatment) in addition to 26.2% of un-treated wood meal. The contribution of lignin to the formation of pyrolysis residue was made clear. Interestingly, the increase of lignin content by periodate treatment did not result in the increase of the total yield of aromatic type low molecular pyrolisates. Results obtained here as well as those obtained in our former experiment by the use of chlorite pre-treatment suggested that the formation of pyrolisates is affected not only by the amount of lignin but also by the chemical changes caused during the pretreatment.

2011-108
コニフェリルアルコール及びシナピルアルコールの熱分解反応特性とリグニン熱分解における役割小竹毅郎，河本晴雄，坂　志朗
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Pyrolytic reactivities of coniferyl alcohol and sinapyl alcoholand their roles in lignin pyrolysis
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Abstract: Pyrolytic β-ether cleavage of dimers gives coniferyl alcohol and sinapyl alcohol, while their yields reported from the isolated lignins are not significant. To clarify this contradiction, pyrolytic reactivities of coniferyl alcohol and sinapyl alcohol were studied under N_2/200-350˚C/5min. As a result, evaporation of coniferyl alcohol was competed with some pyrolytic reactions to form condensation products and Cγ-oxidation (coniferyl aldehyde) and Cγ-reducition (isoeugenol) products at 250-350˚C, where β-ether linkages in dimers are reported to be cleaved. Roe of coniferyl alcohol as a pyrolysis intermediate of lignin was also discussed by the yield (coniferyl alcohol + coniferyl aldehyde + isoeugenol) from sugi (*Cryptomeria japonica*) wood and MWL. The yields were only less than 1.5 wt% under neat conditions, while the yields increased by 1.3 to 4.5 times along with the yields of dimer/trimer fractions in 1,3-diphenoxybenzene which suppressed the condensation reactivity of coniferyl alcohol.

2011-109
リグニンの β-O-4 結合新規選択的開裂法(γ-TTSA 法)の検討(2)—DHP への適用—
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Studies on the selective cleavage method for β-O-4 linkages of lignins (γ-TTSA method)(2)
–Application to lignin model polymer (DHP)–
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Abstract: Application of γ-TTSA method (consisted of four reactions; tosylation, thioetherification, sulfonation, alkali-treatment), which has been proposed as new selective β-O-4 cleavage method, to lignin model polymer (DHP) with various linkages such as β-5, β-β and β-O-4 was investigated. FT-IR and ^{1}H-NMR spectra of the four products suggested that the former three reactions proceeded in DHP as well as in β-O-4 model dimer. HSQC-NMR spectrum of the final product after the alkali-cleavage revealed that β-O-4 linkages were selectively cleaved with the reaction of other linkages such as β-5 and β-β in the last reaction.

2011-110
活性酸素種による糖の水素引き抜き反応における速度論的同位体効果の解析
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Analysis of kinetic isotope effect in hydrogen Abstraction from carbohydrate by active oxygen species
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Abstract: In our previous studies, a clear kinetic isotope effect was observed when a pair of a carbohydrate model compound, methyl β-D-glucopyranoside (MGP), and its deuterated compound at the anomeric or C-2 position, methyl β-D-(1-2H)glucopyranoside or methyl β-D-(2-2H) glucopyranoside, respectively, were reacted with active oxygen species (AOS) generated by reactions of O2 with a phenolic compound, 2,4,6-trimethylphenol (TMPh), under oxygen delignification conditions. This result indicates that the AOS **Abstract** the hydrogens connected to the anomeric and C-2 positions of MGP. Contrarily, no clear kinetic isotope effect was observed when AOS were generated by reactions of O2 with another phenolic compound, 4-hydroxy-3- methoxybenzyl alcohol (vanillyl alcohol, VA), and hence, the Abstraction of the hydrogens could not be confirmed in this case. In this study, a pair of MGP and its completely deuterated compound at all the positions, (2H3)methyl β-D-(1,2,3,4,5,6,6-$^{2}H_{7}$)glucopyranoside, was reacted with AOS generated from TMPh or VA under oxygen delignification conditions to examine whether a clear kinetic isotope effect is always observed when AOS **Abstract** one of the hydrogens from the C-H bonds in MGP. A clear kinetic isotope effect was observed in each system of the AOS generators, which shows that AOS generated both from TMPh and VA certainly **Abstract** the hydrogens from the C-H bonds in MGP. We further discuss on the appearance of kinetic isotope effect in the following text.

2011-111

アルカリ蒸解過程におけるリグニン β-O-4 結合開裂の速度論的検討（2）—芳香核構造および側鎖立体構造の影響—

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Kinetic analysis of the β-O-4 bond cleavage of lignin during alkaline cooking process (2)
Effect of aromatic structure and stereo structure of side chain.

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Abstract: In this study, it was examined how the aromatic structure and the stereo structure of side chain of non-phenolic β-O-4 type unit in lignin control the rate of the β-O-4 bond cleavage during alkaline cooking using the *erythro* and *threo* isomers of non-phenolic model compounds, 2-(methoxyphenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (VG), 2-(2,6-dimethoxyphenoxy) -1-(3,4-dimethoxyphenyl)propane-1,3-diol (VS), and 2-(methoxyphenoxy)-1-(3,4,5-trimethoxy- phenyl) propane-1,3-diol (SG). The disappearances of all the compounds used were well approximated to pseudo-first-order reactions. The rate constants (*k*) of the *erythro* isomers of all the compounds were about 4 times as large as those of the corresponding *threo* isomers. The both isomers of VS disappeared much faster than those of VG. On the other hand, SG degraded only slightly faster than VG in any case. These results suggest that the effect of the substitution of syringyl nucleus for guaiacyl nucleus on the rate of the β-O-4 bond cleavage appears more strongly when syringyl nucleus exists as the cleaving phenoxyl ether than when it is present as the carbon framework. Number of peaks observed in the HPLC chromatograms was larger when the mixtures obtained from the *threo* isomers of all the compounds were analyzed than when those from the corresponding *erythro* isomers were analyzed. This suggests that the mechanism of the β-O-4 bond cleavage of *threo* isomer is not completely the same with that of *erythro* counterpart.

2011-112

Effects of DMSO/LiCl dissolution on the structural characteristics of rice straw lignin

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Abstract: Four samples of rice straw (stem only, stem with knot, leaf including sheath, whole straw) were subjected to the dissolution in DMSO/LiCl after the planetary ball milling pretreatment. Regenerated materials from the DMSO/LiCl solution or suspension were treated by cellulolytic enzymes. The samples were almost completely dissolved in DMSO/LiCl by 1 h ball milling. The chemical nature of the regenerated materials and their residue after the enzymatic hydrolysis were analyzed and the accessibility of this rice straw to the enzymatic hydrolysis was evaluated.

2011-113

One electron oxidation of wood and carbohydrates

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Abstract: One electron oxidation of lignocellulosic materials can give a material with self bonding properties on further pressing and heating. Similar oxidation gives wet strength properties to paper after short heating. One electron oxidation of lignocelluloses materials are complicated reactions and both oxidized lignin and carbohydrates can contribute to the bonding ability. This paper present results pointing to that oxidized carbohydrates of the dialdehyde type plays an important role in the bonding.

2011-114

酸性サルファイトパルプ残留リグニンがパルプの酵素糖化挙動に及ぼす影響

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Effect of residual lignin in acid sulfite pulp on behavior of enzymatic saccharification of pulp

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Abstract: The lignin contents of pulp with enzyme impregnated and amounts of the enzyme in pulp were analyzed by the acetyl bromide method and the K number method to establish a method for estimating amounts of enzyme adsorbed to residual lignin in the enzyme-treated pulps. The estimation is very important to develop a highly efficient enzyme-hydrolysis of ligno-cellulosics materials for bio-ethanol production. When lignin analysis was conducted by the acetyl bromide method, the apparent lignin content of pulp with impregnation of 12.7 FPU of enzyme per one gram of pulp was about 9%, which was only 1% point higher than the lignin content of pulp (7.9%). The apparent K numbers of pulp increased with the amounts of enzyme impregnated in pulp. However, the apparent K numbers of the pulp residues decreased during the enzymatic treatment of pulps. The residual lignin of the pulps, which were less soluble in water, partly liberated from the pulps during the enzymatic treatment. In addition, a part of reducing sugars in the hydrolysate must consume the permanganate of the K number method. It is still difficult to establish it, and therefore the both methods are discussed in comparison with the pyrolysis-gas chromatography/ mass spectrometry (Py-GC/MS) method.

2011-115

Sulfurous acid treatment of wood

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Abstract: From the wood bio-refinery's point of view, now, sulfurous acid treatment is still attractive because not only lignin is effectively removed but also hemicelluloses can be hydrolyzed to monosaccharides during the treatment. So in this work, first, in order to understand the basic behavior of hemicelluloses during the dilute acid treatment, hydrolysis of Radiata Pine (RP) with dilute hydrochloric acid, sulfuric acid and sulfurous acid was conducted. Main concern was whether or not it is possible to convert as much hemicelluloses as possible into monosaccharides while depressing the further degradation of produced monosaccharides and cellulose degradation. Under the condition examined, the highest yield of each monosaccharide from hemicelluloses were as follows: mannose 87%, xylose 96%, galactose 85%, and, arabinose 98%. Second, in order to know degradation of monosaccharide in these acids, model degradation experiment was conducted. The results showed that, compared with that in HCl and in H_2SO_4, degradation of each monosaccharide in sulfurous acid hardly changes significantly with increase of acid concentration. In a word, sulfurous acid treatment seems to be of benefit to bio-refinery from hemicellulose.

2011-116

リグニン性状の水蒸気爆砕条件依存性

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Effect of the steam-explosion conditions on cedar-lignin properties

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Abstract: It is required that a more sustainable society is realized by promoting global production that reduces the environmental burden of a product throughout its life cycle. We are currently researching the use of woody biomass, particularly the application of woody lignin to the epoxy resin widely used in modern electric and electronic equipment. It is preferable that the lignin has homogeneous properties when we apply it to electric and electronic devices. We have investigated the variability and dependence of lignin properties on steam-explosion conditions. The molecular weight of lignin after steam-explosion process decreased by setting the steam pressure higher and the steam time longer. However, the hydroxyl equivalent of the lignin increased under those conditions. There was less variability in the properties of the lignin obtained by steam- explosion, that is, the steam-explosion method is the manufacturing system which can produce the lignin that have homogenous properties.

2011-117

バイオエタノール製造副産リグニンを利用したコンクリート用化学混和剤の製造

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Production of concrete chemical admixture based on byproduct lignin of the woody bio-ethanol process

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Abstract: Bio-ethanol production using soft wood resources is an important national challenging issue related to the nation resource sufficiency due to the accumulating soft wood biomass in Japan. FFPRI is producing woody bio-ethanol from Japanese cedar wood in a pilot research plant on the enzyme saccharification method following the soda cooking. In the pilot process, lignin is separated into a soda solution that is so called black liquor. We are trying to find an applicable method of producing highly value added materials using by-product lignin, because producing highly value added by-products could very much accelerate the forthcoming commercial production of woody bio-ethanol. A simple method to produce amphiphilic lignins that is highly valued added functional material was studied using glycidylethers on the single reaction step in the black liquor. Concrete admixtures such as water reducing agent were produced by purifying the reacted amphiphilic lignin mixture. The performance of the produced concrete admixture as water reducing agent was 3 times higher than widely used commercial product. The admixture had enough quality on the concrete mortar strength test. The admixture showed sufficient performance of concrete air entraining agent as well.

2011-118

バイオディーゼル燃料用植物の有効成分の探索

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Investigation of effective ingredients from a plant for biodiesel fuel production

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Abstract: *Jatropha curcas* L. is, native to tropical Latin America, an oil-bearing shrub widely harvested in tropical and sub-tropical regions throughout Africa and Asia. The plant is resistant to drought and diseases and can grow on wastelands or barrens. The seed contain about 30% oil with a fatty acid composition similar to that of palm oil. The seed oil contains toxic compounds for humans and its nutritional utilizations are impossible. For these reasons this non-edible oil from *J. curcas* is favored for biodiesel fuel production. Although irritant phorbol esters were isolated from *J. curcas,* the other chemical constituents of *J. curcas* were not fully understood. In the study, we found antioxidant activity of some extracts from the defatted seed residue of *J. curcas*. From the active extracts, one lignan and two neolignans with catechol moieties were isolated and identified. Antioxidant activity of those compounds was also found.

2011-特別講演

リグニン研究・教育五十年、「意気に感ず」

荻山紘一
山形大学名誉教授

Outlook of my study and education about woods for fifty years" Heart to heart"

Koichi Ogiyama
Professor Emeritus of Yamagata University

Abstract: My study of wood and forest from chemical viewpoint of components have been for ca.50-years. I am now going to outline several studies briefly and discuss with some criticisms and many renections. Main subjects are as follows, 1) Lignin structure and reaction on the nitric acid oxidation, 2) Manufacturing cellulosic pulp by non-aqueous solvent system, 3) Chemosystematic investigation of Sugi (*Cryptomerla japonica*) on the basis of heartwood or foliage extractives (diterpene, wax and phenols), 4) Chemosystematic investigation of Japanese Percimmon, Kaki (*Diospyros kaki*) on the basis of isozyme pheno-types, 5) Physiologically active compounds; plant hormones in sugi foliage, 6) Biologically active compounds of extractives of domestic wood species (*Pinus densiflora, Cryptomeria japonica, Taxodium disticum* etc.), 7) Biologically active compounds of tropical heartwood extractives (*Dalbergia latifolia, Artocarpus heterophylla, Macherium pedicellatum* etc.). From viewpoint of forest chemistry, importance of sense about the fate of tree components will be pointed out to maintain the sound forest.

2011-201

バクテリアにおけるリグニン由来ビフェニル化合物の脱メチルシステム

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Characterization of the O demethylation system essential for the catabolism of a lignin-derived biphenyl compound in *Sphingobium* sp. strain SYK-6

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Abstract: *Sphingobium* sp. strain SYK-6, a bacterial degrader of various lignin-derived biaryls and monoaryls, is able to grow on 5,5'-dehydrodivanillate (DDVA). In a previous study, *ligX*, which shows the similarity with the oxygenase component gene (*vanA*) of vanillate demethylase of *Pseudomonas putida*, was isolated as the gene involved in the O demethylation of DDVA. However, genes for electron transfer components have not yet been identified. From the genome sequence of SYK-6, we found two ferredoxin genes and two ferredoxin reductase genes as the candidate genes for electron transfer components. Disruption of each gene indicated that SS1C_Con002_0548 (ferredoxin) and SS1C_Con009_0377 (ferredoxin reductase) were essential for the growth of SYK-6 on DDVA. A mixture of crude enzymes containing the gene products of *ligX*, SS1C_Con002_0548, and SS1C_Con009_0377 produced in *Escherichia coli* catalyzed the O demethylation of DDVA in the presence of NADH. It was concluded that the DDVA *O*-demethylase system consists of an oxygenase component, a ferredoxin, and a ferredoxin reductase.

2011-202

Biodegradation of heptachlor and its metabolites in contaminated soil by white-rot fungi

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Abstract: The ability of white-rot fungi (WRF) to degrade heptachlor and heptachlor epoxide has been investigated. During 14 days incubation, heptachlor was transformed completely to chlordene, heptachlor epoxide and 1-hydoxychlordene by *Pleurotus ostreatus* (hiratake) in PDB and Kirk's high nitrogen (HN) media, indicating hiratake has better ability rather than *Phlebia* fungi. For application purpose, spent mushroom waste (SMW) of hiratake and/or fungal substrates of *Phlebia* was used. After 28 days incubation, approximately 89% and 100% of heptachlor was eliminated by hiratake SMW and *P. acanthocystis* fungal substrate. Chlordene, heptachlor epoxide and 1-hydoxychlordene were detected as metabolites from hiratake SMW while only heptachlor epoxide was detected from *P. acanthocystis* fungal substrate. Since hiratake SMW can degrade heptachlor and heptachlor epoxide, hiratake SMW was applied to treat heptachlor in artificially contaminated soil. Approximately 89% and 92% of heptachlor was eliminated in sterilized (SL) and un-sterilized (USL) soils, respectively. Furthermore, approximately 23% of heptachlor epoxide was eliminated in SL soil. This study demonstrates that hiratake SMW was applicable for degradation of heptachlor and its resistant metabolite, heptachlor epoxide, in contaminated soil.

2011-203

Degradation of aliphatic hydrocarbons in three types of crude oil by *Fusarium* sp. F092 in sea water liquid medium

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Abstract: The capabilities of *Fusarium* sp. F092 to degrade the aliphatic fraction in comparison of three types of crude oil in sea water liquid cultures were examined. The results showed that *Fusarium* sp. F092 having the ability to degrade the aliphatic fraction in crude oil contaminating a liquid culture with artificial sea water (35o/oo). The aliphatic fraction was large in crude oil type-3 than crude oil type-1 or type-2 and the other fractions comprised less than 31% of the total. Crude oil type-1, type-2 and type-3 contained C13 to C31, C13 to C27 and C12 to C20, respectively. F092 showed the best performance to break down the aliphatic fraction in crude oil type-3 (98%) and type-2 (72%) and type-1 (49%) after 60 days at an initial concentration of 1000 mg L-1. Furthermore, almost all the aliphatic compounds (Up to C31) in the crude oil were degraded by F092 which preferred short and long chain hydrocarbons. Incubation of crude oil at concentration of 15000 mg L-1 degraded less than 40% of the aliphatic fraction of all crude oils tested.

2011-204

高機能性微生物による木質バイオリファイナリー、 ～新規リグニン分解特異的プロモーターに関する研究～

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Woody biorefinery with functional microorganisms

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Abstract: In our previous reports, we identified protein (BUNA2) as a strong and sharp spot from hyper lignin-degrading fungus *Phanerochaete sordida* YK-624 under wood-rotting condition by two-dimensional gel electrophoresis, and BUNA2 gene (*bee2*) and a promoter region of *bee2* were cloned by several PCR series. Moreover, *bee2* promoter was used to drive the expression of manganese peroxidase gene (*mnp4*) in *P. sordida* YK-624, and most of transformants showed higher ligninolytic activity and selectively than wild type. BUNA 2 was classified as oxidoredutases containing Zn-binding site. *bee2* was induced by the addition of vanillin, Mn(II), bisphenol A, and veratryl alcohol. Recently, we constructed the various EGFP-expression plasmids which were regulated by various-length *bee2* promoter in order to determine actual promoter region of *bee2* and to modify the promoter.

2011-205

高機能性微生物による木質バイオリファイナリー、 ～白色腐朽菌 *Phlebia* sp. MG-60 株によるセルロースの直接エタノール発酵～

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Woody biorefinery with functional microorganisms ～Direct ethanol production from cellulosic materials by white-rot fungus *Phlebia* sp. MG-60～

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Abstract: Twelve strains of basidiomycetes were applied for ethanol fermentation. Silicon rubber plug was used to block the aeration for keeping semi-aerobic condition in flasks. When glucose was used as carbon source, *Phlebia* sp. MG-60 showed the high productivity of ethanol (over 70% of theoretical conversion rate). When *Phlebia* sp. MG-60 was cultured with in 20 g/l microcrystalline cellulose, 2.8 g/l ethanol, 25.3% of theoretical maximum was detected after 480 h incubation. When silico plug was used for keeping aerobic condition, there was no production of ethanol in the culture with glucose or cellulose. Hexoses; glucose, mannose, galactose and fructose were well assimilated by *Phlebia* sp. MG-60. In the case of pentoses, there was no production of ethanol from arabinose, however, good fermentability of xylose by *Phlebia* sp. MG-60 was observed. When *Phlebia* sp. MG-60 was cultured with in 20 g/l unbleached hardwood kraft pulp (UHKP), 64.3% and 70.3% ethanol of theoretical maximum were detected after 240 h and 480 h incubation respectively. When *Phlebia* sp. MG-60 was cultured with in 20 g/l softwood kraft pulp (USKP), 19.4% and 42.4% ethanol of theoretical maximum were detected after 240 h and 480 h incubation respectively. These results indicated that ethanol production is occurred simultaneously with hydrolysis of cellulose.

2011-206

高機能性微生物による木質バイオリファイナリー
～メタゲノムライブラリからの木材分解酵素獲得の試み～

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Developments of wood biorefinery techniques with functional microorganisms, Functional screening of novel wood-degrading enzymes genes from metagenome libraries derived from soils

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Abstract: Several metagenomic libraries were constructed from soils via short-term enrichment culture. The cultures for accumulation contained avicel, kraft pulp or cedar wood powder as carbon source and the cultures were incubated for a week. Bacterial cells were collected by centrifugation, and whole genomes were extracted. Partial digested (using *Sau*3AI) genomes were ligated into pUC19 plasmid, and then transformed into *Escherichia coli* DH5 α chemical competent cells. Recombinant cells were spread on LB agar medium containing RBBR-stained CMC. After incubation, CMCase-positive clones appeared with clear halo against blue culture color. DNA sequence analysis of the transformed inserts revealed that the sequence contained novel CMCase.

2011-207

高分子リグニン酸化能をもつ CWPO-C における基質酸化部位の同定

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Oxidation mechanism of cationic cell-wall-bound peroxidase (CWPO-C) toward lignin model compounds

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Abstract: Cationic cell-wall-bound peroxidase (CWPO-C) has the capability to oxidize sinapyl alcohol, ferrocytochrome *c*, and synthetic lignin polymers, unlike most peroxidases. It is extrapolated that the oxidation site is located on CWPO-C protein surface and homology modeling and chemically modified CWPO-C studies suggest Tyr-74 and/or Tyr-177 are possible participants in the catalytic site. The present study clarifies the importance of these tyrosine residues for substrate oxidation using recombinant CWPO-C and recombinant mutant CWPO-C with phenylalanine substitution(s) for tyrosine. Our results indicated that Tyr-74 and Tyr-177, instead of heme pocket, take a central role in the oxidation of guaiacol, 2,6-dimethoxyphenol and syringaldazine.

2011-208

シロイヌナズナ CWPO-C ホモログのダブルノックアウト変異体解析

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Function analysis of cationic cell-wall-bound peroxidase (CWPO-C) homolog double-knockout mutants on Lignin in *Arabidopsis thaliana*

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Abstract: Cationic cell-wall-bound peroxidase (CWPO-C) oxidizes sinapyl alcohol and synthetic lignin polymer,and Tyr-74 and -177 located on the protein surface are possible substrate oxidation sites for high molecular weight substrates. These characteristics imply that CWPO-C is related to lignification. Three CWPO-C homolog genes among 73 *Arabidopsis* peroxidases are also suggested to be involved in lignification by the analyses of *Arabidopsis* T-DNA insertion mutants. These results suggest that the Tyr located on the protein surface of peroxidase may play an important role in lignification. In this study, *Arabidopsis* double knockout mutants, in which CWPO-C homolog genes were ablated, were generated to clarify the function of three peroxidases in lignification. Also, protein structures of all *Arabidopsis* peroxidases were constructed by homology modeling, and possible substrate oxidation site locates on protein surface were analyzed *in silico*.

2011-209

Sphingobium sp. SYK-6 株由来の *ligD* 遺伝子を発現する組換え植物の解析

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Characterization of transgenic plants with *ligD* gene isolated from Sphingobium sp. SYK-6

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Abstract: *Sphingobium* sp. SYK-6, a gram-negative bacterium, can utilize various monomeric and dimeric aromatic compounds, which appeared in lignin biosynthetic pathway, such as cinnamic acids, cinnamaldehydes and β-O-4 dimers. In our previous studies, some genes involved in degradation of these compounds were isolated from the bacterium and characterized. One of them, *ligD* gene encoding Cαdehydrogenase catalyzes the first step of cleavage reactions for ether bond of β-O-4 dimers. This enzyme oxidizes alcohol to carbonyl group at benzyl (Cα) position of the dimers. It has been known that the presence of carbonyl group at the benzyl position of aryl propane units in lignin speeds up the rate of cleavage of beta-aryl ether linkages during kraft pulping condition (Gierer et al., 1980; Gierer and Noren, 1982). Thus, we introduced the *ligD* gene into plant genome and try to generate transgenic plants whose lignin can be easy to remove from hollocellulose fraction under the alkaline pulping condition. The enhanced cleavage of beta-aryl ether linkages which are the most common bonds in lignin structure might contribute not only to pulp and paper industries but also to bioethanol production from lignocellulose materials. Characteristics of the transgenic *Arabidopsis* plants will be discussed as a preliminary step toward the molecular engineering of lignin.

2011-210

イネにおけるシリンギルリグニン生合成経路の解明

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Elucidation of syringyl lignin biosynthetic pathway in rice plant

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Abstract: We have analyzed the physiological function of putative rice (*Oryza sativa*) caffeic acid *O*-methyltransferase 3 (OsCOMT3). Recombinant COMT3 catalyzed the 5-methylation of 5-hydroxyferulate (5-HFA) and 5-hydroxyconiferylaldehyde (5-HCAld) as substrates, and the methylation of 5-HFA was inhibited by 5-HCAld. The rice plant which was down-regulated in expression of *COMT3* exhibited a weakened staining with Wiesner reagent in the walls of vascular bundle cells and sclerenchyma tissue compared to wild-type plant. Lignin content of the transgenic shoot was decreased, and syringyl lignin content of those was reduced up to 87% than that of wild-type. These data indicate that the physiological function of COMT3 is to catalyze the 5-methylation in the biosynthetic pathway of syringyl lignin, and suggest that the biosynthetic pathway of syringyl lignin in rice is similar to those in dicotyledonous plants.

2011-P01

シラカシモデル林における土壌形成過程での有機物の挙動

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Changes of organic substances at *Quercus myrsinaefolia* forests during soil formation

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Abstract: Lignin is considered to play an important role in the fixation of organic carbon on the earth. On the other hand, it is difficult to trace quantitatively the behavior of lignin during soil formation. In this study, changes of organic substances during soil formation were investigated in terms of organic carbon content, extractability by various solvents and yield of Klason residue.

Samples (living plant, litter and soil) were collected at *Quercus myrsinaefolia* forests at the University of Tokyo Tanashi Forest. Total organic carbon (TOC) of living wood and litter were among 43–47%. TOC of soils were 14-4% and was in a range of carbon (C) contents of Japanese forest soil. Any soil did not contain inorganic carbon. This means that C content is equal to TOC in Tanashi forest soil. Amounts of organic matter were estimated by assuming that the carbon content of organic matter was 50%. Yields of extractives on estimated organic matter were 10–38%, 3–11% and 1-3% in living wood, litter and soil, respectively. It was apparent that organic matter turns into hardly extractable materials during soil formation.

2011-P02

Chemical components of eccentric grown wood of teak

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Abstract: Chemical components of minimum and maximum ring width in the outer heartwood of eccentric grown teak (*Tectona grandis*) were compared. The woods were sampled from 10 leaning trees of thinning activities. The values of chemical components of eccentric wood were in the range of normal teak woods. *T-test* analysis showed that no significant differences in extractive, ash, pentosan, and acid soluble lignin content levels. However, the difference was found in Klason lignin content, which the woods with maximum ring width showed higher values than those of minimum ring width.

2011-P03

植物の進化に伴うリグニン構造の多様化に関する考察

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Speculations on the diversification of lignin structure during the evolution of plant

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Abstract: Diversification of lignin structure occurred during evolution of plant, from *p*-hydroxyphenyl

(H)-guaiacyl (G) lignin to syringyl (S)-G lignin. About 400 million years ago, the first vascular plants appeared on the earth. The vascular bundle performed various functions, conduction of aqueous material, mechanical support of plant, and defense against injuries and microbial attack by formation of supra- molecular complex composed of lignin and polysaccharides. Pteridophyta and gymnosperms were the first dominant vascular plant, but change of environment on the earth resulted in evolution of angiosperms, in which multifunctional tracheid differentiated to conduction- specialized vessel and support-specialized fiber. The strong defense function arising from the frequent condensed structures in H-G lignin in gymnosperms was weakened to moderate defense by less condensed S-G lignin in angiosperms. Adequate defense by S-G lignin and quick biodegradation after the plant death provided suitable environment for frequent alternation of generation and faster evolution to adapt environmental change on the earth.

2011-P04

針葉樹仮道管壁複合中間層におけるリグニン-多糖類-超分子複合体の形成に関する考察

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Speculations on the formation of supramolecular complex of lignin and polysaccharides in the compound middle lamella region of softwood tracheid

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Abstract: Supramolecular structure of lignins in compound middle lamella (CML) and secondary wall (SW) of softwood tracheid differs partly due to higher content of condensed structures (5-5′-biphenyl, dibenzodioxocin and 4-O-5′-diphenyl ether) in CML lignin than in SW lignin. In an early stage of cell wall formation, random networks made up of cellulose microfibril, xyloglucan and pectin are formed in CML. A large number of globular *p*-hydroxyphenyl-guaiacyl lignin grow on the network. The growing ends of folded chain molecules are on the surface of the globules, and successive addition of monolignols by β-O-4 and β-5 linkages are prevailed. When the space on the polysaccharide network is almost filled up, insufficient space for further monolignol addition causes frequent bonding between two growing ends by 5-5′ or 4-O-5′ linkages. The circadian rhythm of cell activity may accelerate closer contact of the globules, and supply of one monolignol after the 5-5′ bonding to form dibenzodioxocin structure.

2011-P05

広葉樹の葉リグニンの DFRC 法による検出（1）

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Detection of broad-leaf lignin in angiosperms by DFRC analysis (1)

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Abstract: The DFRC analysis gives C6-C3 type degradation products from arylether linkages of lignin. Therefore this method can be used to detect lignin specifically from plant tissues, excluding other (poly)phenolic substances. To investigate the lignin composition in broad-leaves of angiosperms, DFRC analysis was employed. Many leaves gave both guaiacyl- and syringyl-type degradation products, which indicates the broad leaf lignin has common structural elements with xylem lignin of the same tree. However, results were not always the same among species and tissues. Syringyl / guaiacyl ratio of DFRC products of leaf lignin was apparently lower than that of xylem lignin. The leaves of persimmon and cherry gave only trace amount of degradation products. These results show the heterogeneous distribution of leaf lignin in angiospermous trees.

2011-P06

ニトロベンゼン酸化法によるリグニンのビフェニル型構造の定量的検討

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Quantitative evaluation of biphenyl type structures in lignin by nitrobenzene oxidation method

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Abstract: Japanese cedar wood meals were subjected to alkaline nitrobenzene oxidation at different reaction temperature and for different period to investigate the yields of dehydrodivanillin, dehydrovanillinvanillic acid and dehydrodivanillic acid that are considered to be the products from biphenyl type structures (5-5 linkage type) in lignin. On the basis of the total yield of the products obtained in the optimized reaction condition, 170 ºC for 2 hours, it was suggested that at least 5.2 % of phenylpropane units in the cedar lignin were involved in 5–5 linkage type structures.

2011-P07

パーム油由来のグリセリンを利用したポリウレタン複合材料及びエポキシ樹脂の熱的・機械的性質

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Thermal and mechanical properties of polyurethane composites and epoxy resins derived from glycerol from palm oil

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Abstract: Polyurethane composites were prepared using industrial by-products such as lignin (LS) obtained in pulping process, molasses (ML) obtained in sugar production process, crude glycerol (CG) obtained in bio-diesel fuel production process, cellulose and empty fruit bunches (EFB) of oil palm. Sodium lignosulfonate (LS) , ML and CG were dissolved in polyethylene glycol 200 (PEG), and each of the above solutions, LSP, MLP and CGP were obtained. Cellulose powder with different particle size and EFB powder were mixed with the mixture of the above polyols, and then the obtained mixtures were allowed to react with poly(phenylelnemethlylene)polyisocyanate (MDI) under a pressure of 20 MPa for 1 h, and then at 120 ºC, for 2 h. The mechanical properties were studied by bending tests. The bending strength (σ) was almost constant regardless of MLP contents (MLP content, % = $W_{MLP}/ W_{MPL} + W_{LSP}$). Maximum value of σ_{max} was 23 MPa when fiber length was 28μm at MLP content of 80%, while σ_{min} was 11 MPa when fiber length was 37 μm at MLP content of 50 %. The bending modulus *E* values also showed the similar tendency to those of σ values. Crude glycerol and pure glycerol were allowed to react with succinic anhydride, respectively. When the obtained poly acid derivatives of crude glycerol (CGPA) and GPA were allowed to react with glycerol diglycidyl ether (GDGE), the weight contents of CGPA $\{W_{CGPA}/(W_{CGPA}+W_{GPA})\}$ were change from 0 to 100 %. The glass transition temperatures were almost constant regardless of CGPA contents in epoxy resins.

2011-P08

工業リグニンを用いた新規セメント分散剤の開発

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Preparation of novel lignin-based cement dispersants from technical lignin

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Abstract: We have developed amphiphilic lignin derivatives from technical lignin by the reaction with poly(ethylene glycol) derivatives. They obviously showed considerable surface activity. The utility of amphiphilic lignin derivatives were evaluated in terms of their dispersion capacity, as a cement admixture. Amphiphilic lignin derivatives (EPEG) prepared with monoepoxylated poly(ethylene glycol) gave higher dispersity to cement than lignosulfonate (LS), a commercially available lignin, at room temperature and 6ºC. The cured cement mixed with amphiphilic lignin derivatives at both temperatures also revealed almost the same or slightly higher bending strength than those with LS and without lignin-based additive. In conclusion, EPEG-based amphiphilic lignin derivatives were proven to be a promising cement admixture that would be available even in the wintertime.

2011-P09

リグニン誘導体を用いた天然型有機系紫外線吸収剤

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Natural organic ultraviolet absorbers from lignin derivatives

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Abstract: Currently, ultraviolet (UV) absorbers are becoming popular due to cosmetic and medical purposes. Exposure of skins to UV rays from the sun causes damage of the skins. Excessive exposure induces skin cancer and aging. Although the demand for UV absorbers with high safety and minimum environmental impacts is becoming increasing, most of the organic UV absorbers currently available are synthetic compounds from petroleum. Therefore, we started the research to develop UV absorbers from natural organic compounds. Natural aromatic polymer, lignin retain the potential to produce strong UV absorbers by oxidative degradation. By extensive screening of degradation products from lignin, we found the products having high absorbance in UV-A and UV-B regions.

2011-P10

フェルラ酸およびカフェ酸をモノマーとするポリエステルの高分子量化

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Molecular weight enhancement of polyesters from ferulic or caffeic acids

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Abstract: Enhancement of molecular weight was attempted for polyesters prepared from ferulic (FA) or caffeic (CA) acids, both of which are lignin-related aromatic hydroxyl acids. Polymerization of these acids was performed by ester exchange reaction in sodium acetate/acetic anhydride system followed by polycondensation at different temperatures and reaction time under reduced pressures. Molecular weight (MW) of poly(caffeic acid) (PCA) as estimated by GPC (relative to polyetyrene standard) increased up to 1.0×10^6 by polycondensation at 160 ºC for 16 h. On the other hand, MW of poly(ferulic acid-*co*-glycolic acid) (PFG) increased only up to 8.0×10^3 after polycondensation at 180 ºC for 26 h. These polyesters showed different thermal behaviors: PCA formed liquid crystalline (LC) phase under shear upon heating to 140-170 ºC; PFG polymerized with the FA feed ratio of 30% spontaneously formed LC phase above 130 ºC.

2011-P11

ポリビニルアルコールとの微視的複合化によるリグノスルホン酸のゲル化と機能発現

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Composite gel formation and functionalization of lignosulfonic acid via microcompositions with poly(vinyl alcohol)

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Abstract: Utilization of isolated lignins as a solid material is constrained by poor film formability and insufficient moldability due to their low molecular weight and molecular structure. In the present study, we prepared lignosulfonic acid (LSA)/poly(vinyl alcohol) (PVA) composite hydrogels. Cross-linking moiety was introduced by thermal treatment or reaction with glutaraldehyde. By thermal cross-linking, an elution of LSA in aqueous media could be prevented by formations of hydrogen bonding and sulfonate ester between LSA and PVA, both of which were corroborated by FT-IR measurement. The thermal-treated composite hydrogels demonstrated a sustained-release behavior of nicotine in normal saline solution. On the other hand, pre-interlinking of LSA was performed using poly(ethylene glycol) diglycidyl ether as a linking agent, in order to improve the LSA content for the LSA/PVA composite hydrogel prepared via chemical cross-linking in aqueous media. Thereupon, the incorporation of linked-LSA achieved much improvement of water retentivity for the composite hydrogels, where the maximum retentivity of distilled water was > 500 times its own weight.

2011-P12

アルカリリグニンのアルミニウム毒性除去能に関する研究 ―擬似酸性土壌を用いた系での検討―

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Studies on the ability of alkali lignin to reduce aluminum toxicity assayed using acidic soils

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Abstract: The ability of alkali lignin to reduce aluminum toxicity was assayed by plant growth tests using acidic soils. Acidic soils used in this study were prepared by adding aluminum chloride or hydrochloric acid to Akadama soil (loamy soil). Root elongations of radish were suppressed in these acidic soils, and addition of alkali lignin to these soils did not have any effect on recovery. This result indicates that alkali lignin was not effective at reducing aluminum toxicity when these acidic soils were employed. Preliminary experiment using saponified ozone-treated kraft lignin indicates that improvement of the ability of alkali lignin may need to become effective at reduce aluminum toxicity in these soils.

2011-P13

直パルス通電加熱による木質バイオマスの急速熱分解生成物

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Products from fast pyrolysis of wood biomass by pulse current heating

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Abstract: Fast pyrolysis of wood biomass with pulse current heating in order to get useful co-products from bio-oil and to know the pyrolysis conditions on bio-oil compositions and properties and functions of co-products were examined. The maximum yield of bio-oil was shown at around 500℃. The relationships between the reaction temperature and mass balance, the chemical structure and bio-oil compositions, the organics and ammonia adsorbed on char were discussed. It was suggested about the potential of the catalyst on the yields and properties of the products from fast pyrolysis.

2011-P14

バクテリア由来ピノレジノール変換酵素遺伝子の単離と機能解析

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Isolation and Characterization of the Pinoresinol Reductase Gene of *Sphingobium* sp. Strain SYK-6

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Abstract: Our group aims to control the lignin biosynthesis in plants by using lignin catabolic genes from bacteria. In this study, we isolated and characterized an enzyme gene involved in the transformation of pinoresinol (8-8′ dimer) from *Sphingobium* sp. SYK-6. A cosmid clone which conferred the pinoresinol transformation activity to a host strain *Pseudomonas putida* was isolated. In the 3.5-kb SalI fragment of the cosmid, we found a 948-bp open reading frame (*pinZ*) which has 21% identity with pinoresinol reductase of *Arabidopsis thaliana.* Purified His-tag fused PinZ produced in *Escherichia coli* completely converted a racemic mixture of pinoresinol into lariciresinol and secoisolariciresinol in the presence of NADPH. These results indicated that *pinZ* encodes pinoresinol reductase. Disruption of *pinZ* in SYK-6 demonstrated that this gene is essential for the transformation of pinoresinol.

2011-P15

Sphingobium sp. SYK-6 株から単離されたピノレジノール変換酵素遺伝子 *pinZ* を発現する組換え植物の解析

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Analysis of transgenic plants with the bacterial gene for pinoresinol reductase, *pinZ*, which has been isolated from *Sphingobium* sp. SYK-6

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Abstract: We try to modify lignan and lignin biosyntheses in transgenic plants by expression of various types of bacterial genes for catabolism of aromatic compounds. This study focused on one of the genes, *pinZ,* which encodes pinoresinol reductase that catalyzes the conversion of pinoresinol to lariciresinol. To overexpress the gene efficiency in transgenic plants, we modified codon usage of endogenous *pinZ* gene and constructed an expression vector with the resultant cDNA sequence. Generation of transgenic BY-2 cells and *Arabidopsis thaliana* plants have been performed by traditional *Agrobacterium* mediated transformation procedures. Appropriate level of PinZ activity as it is in recombinant *Escherichia coli* could be detected in crude enzymes prepared from both of the transgenic lines.

2011-P116

Quercus 属外樹皮におけるスベリン芳香族部分の化学構造と生合成

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Chemical structure and biosynthesis of poly phenolic domain of suberin in outre bark of Quercus family

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Abstract: Suberin is one of the main components in outer bark of woody plants, wound healing tissue of higher plants and periderm of underground organs. The insoluble biopolymer is composed of poly aliphatic domain and poly phenolic domain. Although the structure and composition of the poly aliphatic domain were well investigated, those of the poly phenolic domain were unclear. In this study, a β-O-4’ enol ether dimer of methyl ferulate and its derivatives were isolated from methanolysis products of extractive free outer bark of

Quercus suber and Q. variabilis. Dehydrogenative polymerization of feruloyloxy hexadecanoic acid with horseradish peroxidase and H_2O_2 was carried out as a suberin model system. A 5-O-4’ diaryl ether type dimer of the substrate and its derivatives were isolated together with a β-5’ dimer. These results suggest that feruloyloxy fatty acid derivatives are dehydrogenetively polymerized by a peroxidase to give β-O-4’ enol ether structures with β-5’, 5-O-4’ and the other coupling structures, which would form the poly phenolic domain of suberin in the outer bark of Quercus family. Dehydrogenative polymerization of feruloyloxy hexadecanoic acid with Q. variabilis bark crude enzyme is being examined.

2011-P17

シロイヌナズナ T-DNA 挿入変異体を用いたリグニン前駆物質輸送体の絞り込み

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Seeking the candidates of lignin transporter using *Arabidopsis* T-DNA tagged mutants

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Abstract: Lignin biosynthesis proceeds in three steps; biosynthesis, transport, and polymerization of lignin precursors. Though many researches have elucidated the biosynthesis and the polymerization of lignin precursors, their transport mechanism has not been investigated except coniferin transport into vacuole. To identify the transporter of lignin precursor, we selected candidates of transporter genes in *Arabidopsis thaliana* by co-expression analysis. Mature stems of T-DNA tagged mutants of candidate genes were harvested and analyzed their lignin distribution. A T-DNA mutant showed weak Mäule color reaction in iterfascicular fiber. Although lignin content of the mutant was not different from Col-0, S/V ratio was decreased. The candidate of transporter gene may be involved in transport of S lignin precursors.

2011-P18

サリチル酸投与によってシラカンバ幼植物体に誘導される植物免疫に係わるペルオキシダーゼの解析

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Analysis of plant-immunity-related peroxidases induced in Japanese birch plantlets by administration of salicylic acid

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Abstract: Salicylic acid (SA) is known to induce immunity in plants against pathogens through systemic acquired resistance. The present study investigated localization of peroxidase induced in Japanese birch plantlets by administration of SA. Histochemical observation of peroxidase revealed that SA induced peroxidases with higher activity in the wider area around the administered site compared to the controls, suggesting the involvement of these peroxidases in plant immunity. Proteomic analysis was also performed using protein samples prepared from the plantlets treated with SA. As the results, malate dehydrogenase and arginase were detected and identified as the proteins specific to SA treatment.

2011-P19

ファイトアレキシン生産時の *Cupressus lusitanica* 培養細胞のリグニン生成

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Lignin formation at phytoalexin producing Cupressus lusitanica cultured cell

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Abstract: The lignin formation with water stress, mechanical stress, elicitor stress on *Cupressus lusitanica* cultured cell was investigated. By analysis of acidolysis and pyrolysis method on the cells at the incubation time same as phytoalexin production (up to 5 days), only the trace amount of lignin degradation products were detected. No significant change of lignin content was observed on Klason lignin content. Therefore, the cells would response at first for protection from elicitor stress in short time (several days) with low molecular weight phytoalexin such like β-thujaplicin. And then at later phase, lignin formation was completed in the cell wall against various stresses including water stress, mechanical stress and so on.

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2012-101

二段階半流通型加圧熱水処理不溶残渣のリグニン

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Lignin in the residues as treated by two-step semi-flow hot-compressed water

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Abstract: Japanese cedar (*Cryptomeria japonica*) and Japanese beech (*Fagus crenata*) were treated with two-step semi-flow hot-compressed water. The first stage was conducted at 230ºC/10 MPa for 15min and the second stage at 270ºC/10MPa for 15mim. The residues at the first and second stages of Japanese cedar contained 59.7 and 43.1wt% of the original lignin, while these of Japanese beech 50.8 and 23.2wt%, respectively. As hot-compressed water treatment proceeds for the first and second stages, the cell wall was destructed for both species. However, the cell wall of the beech was remarkably destructed, compared with cedar, and in the residue of the second stage, only the middle lamella region remained for beech. On the other hand, for the cedar, the cell wall was not so destructed and its structure was comparatively retained. From these observations and the yield of alkaline nitrobenzene oxidation products, the fiber cell wall of the beech encrusted with syringyl lignin would be more likely to be composed of non-condensed type of lignin, while middle lamella and its cell corner region encrusted with guaiacyl lignin would be largely composed of condensed type of lignin. In the case of cedar, however, the middle lamella region remained even at the end of the second stage, thus must have mainly condensed type lignin. In addition, compared with the beech, the cell wall portion of the cedar must have more condensed type of lignin. Such a difference suggests that the topochemical difference in lignin exists in the residues as treated by hot-compressed water.

Keywords: hot-compressed water, topochemistry, lignin distribution, TEM, UV microscope

2012-102

バイオディーゼル燃料用植物ジャトロファから抗酸化活性を有するカテコール型リグナン・ネオリグナンの単離

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Isolation of antioxidant catechol lignan/neolignans from *Jatropha curcas,* a shrub for biodiesel fuel production

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Abstract: The ethyl acetate soluble fraction of the methanol extract obtained from the defatted seed residue of *Jatropha curcas* had the same potent antioxidant activities as Trolox. From the antioxidant fraction a catechol-type furofuran lignan, (+)-3,3'-bisdemethylpinoresinol; five catechol-type 1,4-benzodioxane neolignans, (-)-isoamericanol A, (+)-americanol A, 9'-*O*-methylisoamericanol A, 9'-*O*-methylamericanol A, and isoamericanin A; and two catechol-type sesquineolignans with furofuran and 1,4-benzodioxane moieties, isoprincepin and princepin were isolated and identified. Potent antioxidant activities of these eight compounds were also confirmed. The ethyl acetate soluble fraction of the methanol extract was found to be more effective than α-tocopherol by the tests for preventing oxidation of commercial salad oil and Jatropha oil and the biodiesel fuels (BDF) derived from the two oils.

2012-103

リグニン性状とリグニン硬化エポキシ樹脂特性の相関

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Correlation between lignin properties and properties of epoxy resin hardened by lignin

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Abstract: We are currently researching the use of woody biomass, particularly the application of lignin extracted from steam-exploded woody biomass to epoxy resin, which is widely used in modern electric and electronic equipment. We have already reported that the weight-average molecular weight (Mw) of lignin after the steam explosion process decreased by setting a higher steam pressure and a longer process time, however, the hydroxyl equivalent of the lignin increased under those conditions. We report that the correlation between lignin properties and properties of epoxy resin hardened by lignin. Epoxy resins hardened by lignin with different Mw showed approximately the same glass transition temperatures (Tg), implying that the crosslink density of hardened resin is not much different in this range of Mw. We also prepared epoxy molding compounds using lignin as a hardener. Steam-explosion conditions of cedar chips were explored, and the molding compounds with lower water absorption were obtained for longer steam time, reflecting the properties of lignin. Mechanical and electrical properties of molding compounds were independent of the steam-explosion conditions.

Keywords: steam explosion, epoxy, resin, crosslink, mechanical property.

2012-104

グリコールエーテル系溶剤中での酸分解によるスギ木粉からのリグニン抽出および抽出リグニンのサーモトロック液晶性ポリエステル化

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Lignin extraction from Sugi (*Cryptomeria japonica* D. Don) woodmeal by acid-catalyzed solvolysis in glycolethers and preparation of thermotropic liquid crystalline polyester from the glycolether lignin

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Abstract: Extraction of Lignin from Sugi (*Cryptomeria japonica* D. Don) by acid-catalyzed solvolysis in glycolethers at 160 °C for 2 h has been performed. The glycol lignin, obtained by concentrating the soluble fraction in glycolethers, showed good solubility to acetone, 2-butanone and chloroform. Furthermore, it was found that the glycol lignin contains considerable amount of hydtoxyl groups (0.677 mmol OH / g). Preparation of polyesters by esterification of the glycol lignin and diacid chlorides (adipoyl chloride, sebacoyl chloride, and terephthaloyl dichloride) was performed in acetone. The polyesters, obtained as the insoluble fraction in acetone, showed melting transitions at 70 °C and 190-210 °C. The multiple melting transition implies that the glycol lignin polyester has the thermotropic liquid crystalline nature, which was shown by polarized optical microscopy.

Keywords: solvolysis lignin, glycolethers, sulfonic acid, liquifaction, liquid crystalline polyesters

2012 特別講演

バイオエタノール製造で副生するリグニンの有効利用

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Utilization of lignin coproduced in the bio-ethanol production process

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Abstract: Lignocellulosic biomass resources, such as wood wastes and oil palm trunks(OPT), are expected to be feedstock for recovering lignin derivatives during 2nd-generation bioethanol production process. In the present study, OPT were thermally extracted with ethyleneglycol and phenol/ ethyleneglycol mixed solvent. The soluble fraction includes mainly lignin derived fraction (LDF), which exhibited the good plasticity and thermal stability. The plasticized fractions were processed to prepare green composites (biomass-derived carbon fibers and biomass plastics).

Keywords: lignocellulosic biomass, oil palm trunks, solvent extraction, ethanol fermentation, lignin

2012-201

MWL 抽出残渣からの LCC 解析用フラクションの探索 (2) :2 次元 NMR による分析

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Fractionation of extracted residue of MWL for LCC analysis (2)

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Abstract: The residual wood meal left after milled wood lignin (MWL) isolation (MWR) was fractionated several times to afford xylan-lignin fraction (X-L). X-L was extracted with lignin solvent 1, 4-dioxane/water (9: 1, v/v) to give a soluble fraction (X-L-Fraction-1 (XL-F1)) and an insoluble fraction (XL-F1-residue). XL-F1-residue was further extracted with xylan solvent (DMSO) to afford a soluble fraction (X-L-Fraction-2 (XL-F2)) with 43.0% yield based on XL-F1-residue. XL-F2 was mainly composed of xylan and some amount of lignin, and according to the 2D NMR analysis, it is suggested the existence of phenyl glycoside type LC linkages in XL-F2.

Keywords: *Eucalyptus globulus*; milled wood lignin (MWL); lignin-carbohydrate complex (LCC); gel permeation chromatograph5y (GPC); hetero-nuclear single quantum coherence (HSQC)

2012-202

^{13}C 標識法と高分解能NMR を組み合わせたリグニンの構造解析

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Structural analysis of lignin by a specific^{13}C-enrichment technique combined with high resolution solution state NMR

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Abstract: In order to analyze lignin structures, a technique of specific ^{13}C-enrichment of cell wall lignin combined with nondestructive analysis of the whole cell wall material by high-resolution 2D-NMR (HSQC) in solution-state has been developed. Additional technique of making difference NMR spectrum between ^{13}C -enriched lignin and unenriched lignin provided a simpler spectrum arising exclusively from the ^{13}C -enriched carbon. From the signal intensity of the simplified difference HSQC spectrum between^{13}C$_{\alpha}$-enriched and unenriched lignins, quantitative determination was made on the frequencies of major inter-unit bonds, and coniferyl alcohol, coniferaldehyde end groups.

2012-203

MALDI-FT-ICR MS/MS による単離リグニンの精密構造解析

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Structural analysis of the isolated lignin by MALDI-FT-ICR MS/MS

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Abstract: MALDI-MS gives direct structural information in a wide range of molecular weight regions. However, **Abstract**: structural analysis of lignin by MALDI-MS is still limited. Our group has analyzed isolated and synthetic lignin using MALDI-TOF and Fourier-transform ion cyclotron resonance (FT-ICR) MS. In this study, structure of the lignin isolated from *Eucalyptus globulus* and *Fagus crenata* was analyzed by MALDI-FT-ICR MS/MS. Comparative analyses of the mass spectra between the isolated lignin and synthetic lignin model compounds demonstrated existence of oligomeric structures including β-β and β-O-4 linkages.

Keywords: interunit linkage, network structure, β-O-4 linkage, syringaresinol,
Eucalyptus globulus, Fagus crenata

2012-204

Lignin released from spruce wood during hot-water extraction

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Abstract. Ground spruce sapwood was extracted with pressurized hot water in an accelerated solvent extractor (ASE) at 170 ºC during 20, 60 and 100 min. Dissolved aromatic substances in water extracts were isolated by sorption on XAD-7 resin and fractionated into lignin, oligomeric aromatic substances (OAS) and insoluble-in-methanol compounds (IMC). The extracted and separated fractions as well as the ground wood before and after extraction were analyzed by classical wet chemistry (Derivatization Followed by Reductive Cleavage (DFRC), Klason lignin and content of extractive substances) and instrumental physico-chemical methods (GC, RP-HPLC and SEC, and NMR, FT-IR, UV and mass spectrometry). The yield of dissolved lignin slightly increased during the hot-water extraction. Simultaneously, the proportion of lignin in extracted total dissolve solids decreased to about the half. The physico-chemical characteristics of isolated lignins were considerably different compared to spruce MWL. The extracted lignin had a notably lower molar mass than MWL. During hot-water extraction the number of hydroxyl and especially carboxylic groups in lignins increased and the lignins became more condensed.

2012-205

アセチルブロミド法によるリグニン含有量の定量におけるタケパルプ中のキシラン含有量の影響(II) フルフラール生成量の検討

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Effect of xylan content in alkali bamboo pulp on determination of lignin content by acetyl bromide method (II) –Examination of furfural production -

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Abstract: The xylan in hardwood pulp affects the acetyl bromide method due to UV absorption of the product. The maximum production of furfural from xylose in the acetyl bromide treatment was 8.5 %. During room temperature treatment, furfural decreased slightly, but UV absorbance of the resulting solution at 280nm increased. On the other hand, in this treatment with heating, furfural decreased remarkably but those of UV absorbance increased slightly. It shows that xylan produces furfural and it promptly changes to product which has UV absorption.

2012-206

リグニン β-O-4 結合新規選択的開裂法(γ-TTSA 法)の検討(4)-天然リグニンへの適用-

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Studies on the selective cleavage method for β-O-4 linkages of lignins (γ-TTSA method) (4) -Application to natural lignin-

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Abstract: Application of γ-TTSA method (consisted of four reactions; tosylation, thioetherification, sulfonation, alkali-treatment), which has been proposed as new selective β-O-4 cleavage method, to Milled Wood Lignin (MWL) from *Eucalyptus globulus*. HSQC-NMR spectra of the four reaction products suggested that the four reactions proceeded in MWL as well as in lignin model compounds. Especially, HSQC-NMR spectrum of the final product revealed that β-O-4 linkages were selectively cleaved with the retention of β-β linkages in the last reaction.

Keywords: Cleavage of β-O-4 linkage, β-Elimination, *Eucalyptus globulus*, HSQC-NMR, LCC, Milled Wood Lignin

2012-207

TEMPOをメディエーターに用いたリグニンモデル化合物の電解酸化

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TEMPO-mediated electro-oxidation of lignin model compounds

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Abstract: The TEMPO-mediated electro-oxidation of monomeric lignin model compound **1G** (1-(4’-ethoxy-3’-methoxyphenyl) ethanol) in 70% CH_3CN-H_2O and 10% dioxane-carbonate buffer afforded the corresponding Cα-carbonyl compound **2G** in high yields, suggesting that the oxidation of Cα-hydroxyl group proceeded efficiently. On the other hand, in the TEMPO-mediated oxidation of dimeric compound **3G** (4-ethoxy-3-methoxyphenylglycerol-β-guaiacyl ether) in 70% CH_3CN-H_2O, most of starting material **3G** was recovered, whereas in that of compound **3G** in 10% dioxane-carbonate buffer, the corresponding Cγ-carbonyl compound **7G** was obtained as a main product in moderate yield, suggesting that the oxidation of Cγ-hydroxyl group proceeded efficiently. As the result, it was found that the TEMPO-mediated electro-oxidation was significantly influenced by the solvent used.

Keyword: 2,2,6,6-tetramethylpiperidine-*N*-oxyl, electrolysis, mediator, lignin , Cα-carbonylation

2012-208

広葉樹リグニン熱分解における低分子シリンゴール類/グアイアコール類の生成挙動

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Formation behaviors of monomeric syringols/guaiacols in pyrolysis of hardwood lignin

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Abstract: Hardwood lignin gives monomeric syringols/guaiacols with various side-chains at 300-350°C, while their pyrolytic formation mechanisms are not well-known. To clarify it, pyrolytic reactivities of sinapyl alcohol (SA) and coniferyl alcohol (CA) were compared first under the condition of N_2/200-350ºC/5min. As a result, pyrolytic products from SA were similar to those from CA, which suggests similar reactions occurring for both compounds. Influences of the addition of a solvent (1,3-diphenoxybenzene) and an H-donor (1,2,3,10b-tetrahydrofluoranthene) on the reactivities of SA and CA suggested that the decomposition reactivity of SA dramatically increase at 350ºC where radical intermediates play important roles. This characteristic feature reduced the monomeric syringols yields significantly at 350ºC under neat condition and in solution from SA and buna milled wood lignin (MWL). The addition of the H-donor increased the monomeric syringols yields greatly, which is explained by the stabilization effect on the intermediate radicals. On the other hand, the monomeric syringols yields from buna wood at 350ºC were much higher from those of buna MWL and sugi (MWL/wood) even without the addition the H-donor. These results indicate that the buna wood pyrolysis at 350ºC produces some H-donors for stabilization of the intermediate radicals from buna lignin.

Keywords: lignin, pyrolysis, mechanism, sinapyl alcohol, monomer formation

2012-209

亜硫酸を用いた前加水分解化学パルプ化法

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Prehydrolysis chemical pulping by the use of sulforous acid

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Abstract: For the total utilization of wood polysaccharides, suitable combination of prehydrolysis stage and chemical pulping (delignification) stage was surveyed., Condition of prehydrolysis by the use of hydrochloric acid, sulfuric acid or sulfurous acid was adjusted so that majority of hemicellulose could be obtained as monosaccharides. Prehydrolysis residue was subjected to chemical pulping under various codition. Pulping of prehydrolysis residues obtained by hydrochloric acid or sulfuric acid were rather difficult under any conditions examined. On the other hand prehydrolysis residue obtained by sulfurous acid were found to be easily delignified by simple alkali cooking and give pulp in rather high yield (42% based on the original wood) with rather high purity as cellulose (about 92%). Monosaccharide yield from hemicellulose during prehydrolysis stage was close to 90%.

2012-210

Biodegradation behavior of petroleum hydrocarbons by *Pestalotiopsis* sp. NG007

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Abstract: The biodegradation of three different petroleum hydrocarbon samples, namely, heavy oil A, heavy oil C and asphalt by *Pestalotiopsis* sp. NG007 was examined under ligninolytic condition at pH 4.5 or under saline condition at pH 8.2. *Pestalotiopsis* sp. NG007 exhibited high activity for the biodegradation of all three petroleum hydrocarbon samples. However, the biodegradability was found to be highly dependent on the type of petroleum hydrocarbons and the environmental condition. The degree of biodegradation of petroleum hydrocarbon components differed according to the petroleum hydrocarbons, the aliphatic fraction being more susceptible to biodegradation than the aromatic, resin, and asphaltene fraction in all petroleum hydrocarbon samples. The extent of biodegradation by *Pestalotiopsis* sp. NG007 was found to be in the order of heavy oil A > heavy oil C > asphalt; the petroleum hydrocarbons with higher composition of aliphatic fraction being more susceptible to biodegradation. Regarding to environmental condition, aliphatic and aromatic fraction was preferentially degraded under saline condition at pH 8.2, particularly in asphalt, led to higher biodegradation rate compared with under ligninolytic condition at pH 4.5. The study shows that the dynamic ratio of aliphatic to other constituents in petroleum hydrocarbons affects the biodegradation behavior by *Pestalotiopsis* sp. NG007.

Keywords: biodegradation, heavy oil, asphalt, hydrocarbon, *Pestalotiopsis* sp., ligninolytic enzymes.

2012-2011

Enhancement of ligninolytic systems for degradation of DDT by *Trametes versicolor* U97 pre-grown in oil palm empty fruit bunch

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Abstract: Oil palm empty fruit bunch (EFB) as agricultural waste is potentially used for pre-grown source of white-rot fungi (WRF) since it contains lignin, cellulose and hemicellulose. Enzyme activity secreted by WRF mainly depends on its additives such as metals and veratryl alcohol. This study aims to investigate the ability of EFB as pre-grown source of *Trametes versicolor* U97 to degrade DDT in liquid medium and soil including addition of several additives e.g. $CuSO_4$, $MnSO_4$, and veratryl alcohol in soil. DDT in water, malt extract liquid medium, and soil was degraded 68%, 75%, and 54% during 30 d incubation period, respectively. Addition of $CuSO_4$ even in low concentration and $MnSO_4$ in high concentration have negative effect for DDT degradation. Furthermore, 0.5 mM of veratryl alcohol was optimum concentration to obtain the maximum degradation. Addition of EDTA as lignin peroxidase (LiP) inhibitor could reduce degradation of DDT, revealed lignin peroxidase plays a role in degradation of DDT.

Keywords: biodegradation, DDT, oil palm empty fruit bunch, *Trametes versicolor* U97, lignin peroxidase.

2012-212

Degradation of 2,4,8-trichlorodibenzofuran, a polychlorinated dibenzofurans, by *Cerrena* sp. F0607

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Abstract: *Cerrena* sp. F0607 was chosen as fungus degrader and degradation of 2,4,8-trichlorodibenzofuras (2,4,8-TCDF) was investigated. The degradation of 2,4,8-TCDF was above 40% after 30 day, the degradation per-unit biomass increased during the incubation period, and glucose consumption increased rapidly when 2,4,8-TCDF was present in the culture. It was evidence that fungus oxidized 2,4,8-TCDF as an alternative source of energy and carbon. The increasing of glucose consumption stimulated the growth of fungi that will couple to the degradation of 2,4,8-TCDF. The ligninolytic enzymes were detected and tent to increase their activity in the presence of 2,4,8-TCDF, especially laccase, manganese peroxidase (MnP) and lignin peroxidase (LiP). The addition of various additives, such as $MnSO_4$, $CdSO_4$, $CuSO_4$, 1-Hydroxybenzotriazole (HBT), NaN_3, $AgNO_3$, and Piperonyl Butoxide (PB) was investigated. The result showed that there were variation on both degradation and enzymatic activities. Through a *Partial Least Square* analysis, it could be clearly concluded that laccase has a role in the degradation of 2,4,8-TCDF. Whereas cytochrome P-450 monooxygenase could not be excluded from the degradation of 2,4,8-TCDF, since PB showed inhibition of the degradation without disturbing fungal growth.

Keywords: biodegradation, 2,4,8-TCDF, *Cerrena* sp., ligninolytic enzymes, oxygenase.

2012-213

高活性リグニン分解菌 *Phanerochaete sordida* YK-624 株における glyoxal oxidase 遺伝子高発現によるリグニン分解特性の改善

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Improvement of ligninolytic properties by high expression of glyoxal oxidase gene in hyper lignin-degrading fungus *Phanerochaete sordida* YK-624

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Abstract: Glyoxal oxidase (GLOX) is a radical copper oxidase that catalyzes the oxidation of aldehydes to carboxylic acids coupled to the dioxygen reduction to H_2O_2. GLOX is a source of the extracellular H_2O_2 that is required for the oxidations catalyzed by the ligninolytic peroxidases. In the present study, GLOX gene (*glx*) of *Phanerochaete chrysosporium* was cloned, and the promoter of *bee2* cloned from *P. sordida* YK-624 was used to drive the expression of *glx*. The expression vector was transformed into a *P. sordida* YK-624 uracil auxotrophic mutant UV-64, and 16 clones were obtained as glx-introducing transformants. These transformants showed higher GLOX activities than wild type of *P. sordida* YK-624 and control transformants into which only marker plasmid was introduced although manganese peroxidase activities of these transformants were hardly different from those of wild type and control transformants. Moreover, these transformants showed higher ligninolytic activity than wild type and control transformants. These results suggest that ligninolytic properties of white-rot fungi can be improved by high expression of *glx*.

2012-214

大腸菌によるポルフィリンの生産と、そのリグニン分解

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Efficient production of porphyrin by *Escherichia coli* and lignin degradation by coproporphyrin

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Abstract: *Escherichia coli* carrying a deletion of ypjD gene produced red pigment, when it is cultivated in minimal A culture medium. This pigment was purified and analyzed by LC/MS, GC/MS, ^{1}H NMR, ^{13}C NMR, and NOESY, and it was assumed to be coproporphyrin(Ⅲ). In order to find a new way to use coproporphyrin, we tried to degrade lignin by photosensitization reaction of coproporphyrin. The absorbance of alkali lignin at 280 nm decreased after photo irradiation at 368 nm with coproporphyrin(Ⅰ).

Keywords: Coproporphyrin, *Escherichia coli*, Lignin degradation, Photosensitizer, Photo irradiation

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2012-215

糸状菌ラッカーゼの至適 pH および速度パラメーターに及ぼす緩衝液中のアミノ基の影響

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Effects of amino group in buffer systems on optimal pH and kinetic parameters of fungal laccase

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Abstract: We found that the optimal pH of fungal laccase from the white rot fungus *Pycnoporus cinnabarinus* varies with buffer systems used in the enzyme reaction. Buffer systems containing amino group (glycine and aspartic acid, tris, and ammonium) caused the optimal pH shifting to alkaline side by 1.5 pH unit for ABTS and by 1.0 pH unit for DMP. There occurred an increase of K_m and a decrease of k_{cat} for ABTS and a decrease of K_m and k_{cat} for DMP in aspartate and tris-acetate buffer system containing amino group. Protonated amino group in the buffer systems seems to affect the optimal pH and kinetic parameters for the laccase.

Keywords: fungal laccase, optimal pH shifting, substrate specificity, substrate binding site, carboxylic acid

2012-216

アオモリヒバのリグナン生合成に関与する *O*-メチルトランスフェラーゼ遺伝子の取得

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Isolation of *Thujopsis dolabrata* var. *hondai O*-metyltransferase involved in the biosynthesis of lignans

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Abstract: *Thujopsis dolabrata* var. *hondai* (Aomori-hiba, Hinoki-asunaro) is one of the useful woods in Japan. Moreover, it is known that *T. dolabrata* var. *hondai* biosynthesizes anti-cancer lignans, such as deoxypodophyllotoxin, β-peltatin and so on. These lignans have 3,4,5-trimethoxylphenyl nuclei, but these oxidative modifications are not present in gymnosperm lignin. Comprehensive genetic analysis by a next generation sequencer is one of the most effective approaches to identify the whole expressed genes in a particular sample, which can help identify the genes involved in the methoxyl substitutions. The aim of this study is to isolate cDNAs which encode enzymes involved in the biosynthesis, especially *O*-methyltransferases (OMTs). As a result, we isolated six OMT genes, *TdOMT 1* to *TdOMT 6.* Currently, we are conducting the heterologous expression of these genes.

Keywords: *O*-methyltransferase; syringyl lignans; biosynthesis; heterologous expression; *Thujopsis dolabrata* var. *hondai*

2012-217

O-Methyltransferases involved in lignan biosynthesis in *Anthriscus sylvestris*

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Abstract: We report the isolation and characterization of two plant *O*-methyltransferases (OMTs) involved in lignan biosynthesis in *Anthtriscus sylvestris*. The recombinant OMTs were overexpressed in *E. coli* expression systems and were tested for activity using a number of substrates. Both OMTs showed exclusive regio-specific activity towards dibenzylbutyrolactone lignans. AsOMT50 converted matairesinol into arctigenin, while AsOMT116 converted thujaplicatin into 5-methylthujaplicatin, and were thus renamed AsMROMT and AsTJOMT, respectively. In a phylogenetic tree generated from an alignment of plant OMT amino acid sequences, AsMROMT and AsTJOMT are located in a clade dominated by plant flavonoid and lignan OMTs. AsMROMT is closely related to the *Carthamus tinctorius* matairesinol OMT (CtMROMT). Gas Chromatography-Mass Spectrometry (GCMS)-based analysis of recombinant AsMROMT and AsTJOMT assays towards their respective substrates show that the two OMTs have comparable kinetic attributes with previously characterized plant OMTs, having $k_{\mathrm{cat}}/K_{\mathrm{m}}$ values of 0.0143 μM^{-1} min^{-1} and 0.0763 μM^{-1} min^{-1}, respectively. Gene expression of the OMTs in different organs show that *AsTJOMT* has highest expression levels in rhizomes, which is in line with previous reports indicating high amount of lignan in the mentioned organ. As for *AsMROMT*, we were unable to observe detectable amounts of its expression in the organs that we tested. To our knowledge, this is the first report of the isolation and characterization of plant OMTs involved in lignan biosynthesis in *A. sylvestris*.

2012-218

Fluorescence-tagged monolignols for delineating plant cell wall lignification

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Abstract: Fluorescence-tagged monolignols, *p*-hydroxycinnamyl alcohols γ-linked to fluorogenic dyes such as aminocoumarin, nitrobenzofuran, or styrylpyridinium derivatives were synthesized and tested as photoprobes for *in vitro* and *in vivo* studies of cell wall lignification. To illustrate the use of the probes for analysis of monolignol-protein interactions, the complexation of each coumarin-tagged monolignol with horseradish apoperoxidase was monitored by Förster resonance energy transfer (FRET). In addition, to test an imaging approach, fluorescence-tagged monolignols were fed into various plant cell systems and the localization of incorporated probes was readily visualized by fluorescence microscopy.

Keywords: enzyme-substrate complex; fluorescence probes; Förster (fluorescence) resonance energy transfer (FRET); *in vivo* imaging; monolignol conjugate synthesis; peroxidase

2012-219

Quercus 属の外樹皮におけるスベリン芳香族部分の化学構造と酵素的生成

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Chemical structure and enzymatic formation of aromatic domain of suberin in outer bark of *Quercus* spp.

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Abstract: To clarify chemical structure of aromatic domain of suberin in outer bark of *Quercus* spp., basic methanolysis of the outer bark of *Quercus suber*, namely cork, with sodium methoxide was performed. From the methanolysis products previously an α=β−*O*−4’ enol ether dimers of methyl ferulate had been isolated and identified, and furthermore the other α=β−*O*−4’ enol ether dimer of a ferulate derivatives was isolated in this study. This ferulate-derivative moiety is presumed to be ω-feruloyloxy(long-chain fatty acids) methyl ester whose the long-chain fatty acids were a mixture of the monologues. A dimeric ferulate bonding to ω-hydroxy(long-chain fatty acids) was isolated for the first time as a methanolysis product, and is considered to be derived from the bonding sites between the aliphatic and aromatic domains. Isolation of a β-5’ benzofuran dimer of methyl ferulate was also suggested. A biosynthetic approach, dehydrogenative dimerization of 16-(feruloyloxy)-hexadecanoic acid with cell-free extracts of *Q. variabilis* bark in the presence of hydrogen peroxide was carried out in order to support the elucidation of the chemical structure. Formation of a 4-*O*-5’ diaryl ether type dimer of the substrate was found for the first time.

Keywords: Cork, *Quercus suber, Quercus variabilis,* ferulic acid, 16-(feruloyloxy)-hexadecanoic acid

2012-220

改変型植物酸性 peroxidase の酵母での発現と精製(4)

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Heterogeneous expression and purification of modified plant peroxidase (4)

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Abstract: Most of plant peroxidases can oxidize coniferyl alcohol efficiently, but not sinapyl alcohol. On the other hand, a few of plant peroxidases were reported to use sinapyl alcohol as preferred substrates. It is sugested that they have the additional active sites in the other positions than the heme pocket in the active site.

We tried to introduce the additional catalytic sites of these peroxidases to PrxA3a, an anionic peroxidase of hybrid aspen, *Populus kitakamiensis*, for substrate specificity modifications and for certifications of the surface amino acid residue hypothesis. As a result, PrxA3a A165W and PrxA3a F77Y, PrxA3a F77Y A165W raised the oxidizing ability of cytochrome *c* which cannot enter into the heme pocket. Furthermore, PrxA3a F77Y, PrxA3a F77Y A165W, and PrxA3a F77Y L182Y gained sinapyl alcohol polymerizing activity. We analyzed shifts of Soret band absorption by H_2O_2 treatment. The responses to the H_2O_2 of Soret band absorption differed in mutated PrxA3a enzymes and wild type. Therefore, it is thought that electron transfer is occurred between heme and mutated amino acid residues.

2012-P01

カンバ類癌腫病菌カバノアナタケ IO-U1 株生菌体による非フェノール性β-*O*-4 型リグニンモデル二量体の分解機構

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Degradation mechanisms of a non-phenolic β-*O*-4 lignin model dimer by intact cells of birch canker-rot fungus *Inonotus obliquus* IO-U1 strain

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Abstract: The present study investigated the degradation mechanisms of a non-phenolic β-*O*-4 lignin model dimer, 1-(4-ethoxy-3-methoxyphenyl)-2-(2,6-dimethoxyphenoxy)-1,3-propanediol, by intact cells of birch canker-rot fungus *Inonotus obliquus* IO-U1 strain. In addition, extracellular ligninolytic enzyme activities of the fungus were assayed with culture liquid based on the modified Basal III medium. The degradation products by β-*O*-4 bond cleavage and by cleavage of Cβ-etherified aromatic ring were detected by GC-MS analysis of the metabolites from the lignin model dimer. The activities of laccase, Mn(II)-dependent peroxidase, and lignin peroxidase were detected as ligninolytic enzymes in the fungal culture liquid. It was suggested that β-*O*-4 bond cleavage and cleavage of Cβ-etherified aromatic ring of the lignin model dimer might have occurred by laccase and unidentified mediators from the fungus, because laccase activity was the highest in the culture liquid.

Keywords: canker-rot fungus, forest pathology, *Inonotus obliquus*, lignin biodegradation, ligninolytic enzyme

2012-P02

イオン液体溶媒系に溶解した植物細胞壁の分子量分布

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Molecular weight distributions of plant cell walls recovered from verious ionic liquid systems

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Abstract: A method for NMR analysis of entire plant cell walls without isolating their components was recently developed in our laboratory. The method consists of ball-milling of cell walls, dissolution in ionic liquids, in situ acetylation, and recovery of acetylated materials. However, dissolution in ionic liquids with relatively long ball-milling times may cause partial degradation of wood components. In order to clarify these points, molecular weight distributions of acetylated plant cell walls recovered from different ionic liquid systems were examined by gel permeation chromatography (GPC). The results showed that the molecular weight of the acetylated cell-walls recovered from 1-allyl-3-methylimidazolium chloride ([Amim]Cl) at 30ºC–80ºC and 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) at 100ºC for 2 h were comparable to or a little higher than that of N-methylimidazole (NMI)/DMSO system.

Keywords: molecular mass, SEC, size exclusion chromatography, lignin, cellulose

2012-P03

アセチル化リグニンを原料とする水酸基を持たないエポキシ樹脂硬化物の合成と熱的性質

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Thermal properties of cured epoxy resins without hydroxyl groups derived from O-acetyl lignin

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Abstract: Cured epoxy resins without hydroxyl groups were prepared using O-acetylalcoholysis lignin (AcAL). AcAL, Bisphenol A diglycidyl ether (BPADGE) and a catalytic amount of 2-ehtyl-4-methylimidazole (2E4MI) were dissolved in tetrahydrofuran (THF), and then THF was removed under a reduced pressure. The obtained reaction mixtures having various [EPOXY]/[PhOAc] mole ratios ranging from 0.8 to 1.2 were cured at 150 ^{o}C for 5 hr. Thermal properties of the obtained cured epoxy resins were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG). The glass transition temperatures (T_g's) showed a maximum at the [EPOXY]/[PhOAc] mole ratio of 1.0. The thermal decomposition temperatures (T_d's) and mass residues at 500 ^{o}C were almost constant regardless of [EPOXY]/[PhOAc] ratios. It was found that 2E4MI acts as an effective catalyst for the curing reaction between PhOAc groups of AcAL and epoxy groups of BPADGE.

Keywords; O-acetyl lignin, cured peoxy resins, sysnthesis, thermal properties.

2012-P04

土壌炭素固定能評価のための植物リターの安定炭素同位体比分析におけるリグニンの影響

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Effect of lignin to stable carbon isotopic analysis of plant litter for the evaluation of soil organic matter accumulation

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Abstract: Stable carbon isotopic analysis of plant litter provides important information for the evaluation of soil organic matter accumulation. The carbon isotope ratio of ^{13}C/^{12}C (δ^{13}C) shows around -14‰ and around -28‰ on the C4 plants and C3 plants, respectively. We have reported that the isotope ratio of soils under the C3 and C4 plants shows convergence to around -24‰ with the depth of the soil increasing. Fresh leafs of the C4 and C3 plants were corrected and the each leave samples were separated in 4 kinds of extractive fractions and Klason lignin fraction. The isotope ratio data of all Klason lignin fraction showed not much difference with that of original plant leafs. The data didn't support of the hypothesis of the leaf lignin that might be a difficult to degrade in soil was the main reason of the carbon isotope ratio convergence with the soil depth.

Keywords: soil analysis, carbon isotope, plant litter, leaf lignin

2012-P05

レジノール型モデル化合物の高圧水蒸気蒸留条件と構造変化の検討

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Examine of condition of high-pressure steam distillation and structural change of resinol model compounds

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Abstract: For determination of high-pressure steam-distillation condition of resinol type compounds from wood, some resinol and dilactone type model compounds such as sesamin, pinoresinol, syringaresinol, dehydrodiferulic acid and dehydrodisinamic acid were synthesized and submitted to the high-pressure steam-distillation at 110℃ to 180℃ with a newly constructed apparatus. Sesamin was distilled at 150℃ but pinoresinol and syringaresinol were not distilled under these conditions. Moreover, when these compounds were heated, these compounds partially changed to each epimers. By contrast dehydrodiferulic acid and dehydrodisinamic acid were not distilled. But 1.4-diphenolic butadiene derivative was distilled by high-pressure steam-distillation. 1.4-Diphenolic butadiene derivative that is degradation product was obtained by decarboxylation of dehydrodiferulic acid and dehydrodisinamic acid.

Keywords: furofuran, furolacton, resinol, ferulic acid, vanillin

2012-P06

リグニンを原料としたポリエステルの調製

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Preparation of polyester derived from lignin

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Abstract: We prepared lignin-based fibrous polyester, by using technical lignin and carboxylic chloride. Kraft lignin (KL) and soda lignin (SL) were used as a technical lignin, while terephthaloyl chloride (TC) was used as a carboxylic chloride. Polyethylene glycol (PEG) 400 and PEG-lignin, an isolated linin recovered from solvolysis process of cedar wood chip with PEG400, were also used to improve mechanical strength of the resulting products. KL- and SL-based polyesters were too fragile to measure the tensile strength, but addition of PEG 400 to SL, and introduction of PEG to lignin showed a little improvement of the tensile strength and lead to thinner diameters of polyester fiber.

Keywords: kraft lignin, soda lignin, PEG-lignin, polyester, tensile strength,

2012-P07

高圧水蒸気蒸留による針葉樹材成分の抽出

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Extraction of constituents from soft wood by high-pressure steam distillation

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Abstract: Newly developed high-pressure steam distillation was conducted for *Thujopsis dorabrate* wood chips by stepwise increasing steam-temperature at 120, 140, 160, 180, and 200℃. Thujopsene was mainly distilled at 120 and 140℃,on the other hand ferrginol was mainly distilled at 160 and 180℃and some degradation products from lignin or polysaccharide such as vanillin and 5-hydroxymethylfurfural were distilled at 200℃.

Keywords: high-pressure steam, steam distillation, extract, soft wood, biomass

2012-P08

Sphingobium sp. SYK-6 株の dehydrodiconiferyl alcohol 代謝系遺伝子の単離と解析

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Characterization of the dehydrodiconiferyl alcohol catabolic genes in *Sphingobium* sp. strain SYK-6

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Abstract: A bacterial catabolic pathway of a phenylcoumaran-type compound, dehydrodiconiferyl alcohol (DCA), was proposed by Habu et al. in 1988. In that pathway, the first step was the oxidation of the alcohol group at the γ-position of the B-ring side chain of DCA into the carboxyl group. The resultant product was degraded to 5-formylferulate and vanillin through the release of γ-carbon and the cleavage of Cα-Cβ linkage of the A-ring side chain. In this study, we isolated and characterized a part of the DCA catabolic genes of *Sphingobium* sp. strain SYK-6. Three alcohol dehydrogenase (ADH) genes, which conferred the DCA oxidation activity on a host strain, were isolated. In a previous study, we isolated three aldehyde dehydrogenase (ALDH) genes from SYK-6, which showed oxidation activities toward a broad range of aromatic aldehydes. All these ALDH gene products oxidized DCA-L into DCA-C. These results suggest that multiple ADH and ALDH genes are involved in the conversion of DCA into DCA-C. Identification of the metabolites of DCA-C suggests that

DCA-C was oxidized to DCA-CL, and then DCA-CL was converted to DCA-S via DCA-CC. The enzyme activity to convert DCA-C into DCA-CL was inducible, and did not require any cofactor.

Keywords: dilignol, β-5, biodegradation, microorganism

2012-P09

ヤマモモおよびオオバヤシャブシの環状ジアリールヘプタノイド生合成遺伝子の検索

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Isolation of cyclic diarylheptanoid synthase genes from *Myrica rubra* and *Alnus sieboldiana*

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Abstract: We have investigated the biosynthesis of a cyclic diarylheptanoid myricanol in *Myrica rubra* by feeding experiments using ^{13}C-labeled cinnamic acid derivatives. On the other hand, we isolated cyclic diarylheptanoids from *Alnus sieboldiana*, which have α-glucosidase inhibitory activity. In the present study, to identify the cyclic diarylheptanoid synthases of *M. rubra* and *A. sieboldiana*, their total RNAs were isolated from young shoots, and analyzed by a next generation sequencer. EST sequences having 70~80% homolog with chalcone synthase (CHS) super family were selected. 5'- and 3'- RACE PCRs were performed using the EST sequences and cDNAs synthesized from total RNAs of *M. rubra* and *A. sieboldiana*.

Keywords: cyclic diarylheptanoids; biosynthesis; transcriptome; *Myrica rubra*; *Alnus sieboldiana*

2012-P10

グリコールエーテル系溶剤中での酸分解によりスギ木粉から抽出したリグニンの沈殿分別と特性化

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Precipitation fractionation and characterization of lignin from sugi (*Cryptomeria japonica* D. Don) extracted by acid-catalyzed solvolysis in glycolethers

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Abstract: Extraction of lignin from sugi woodmeal was performed by solvolysis in mixed glycolethers to which *p*-toluenesulfonic acid was added as catalyst. The solvolysis was performed under reflux at 160 °C for 2 h. Lignin was obtained by concentrating the liquified fraction at 110 °C for 4 h under vacuum. Structural analysis of the obtained lignin was performed by FT-IR, ^{1}H- and ^{13}C-NMR. Furthermore, in order to recover the lignin as solid, precipitation fractionation of the liquified lignin was attempted.

Keywords: solvolysis lignin, glycolethers, sulfonic acid, liquifaction, precipitation fractionation

2012-P11

広葉樹ユリノキあて材の樹幹内におけるリグニンおよび多糖類の偏在性

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Uneven distribution of lignin, cellulose and hemicellulose in the tension wood stem of yellow poplar (*Liriodendron tulipifera*)

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Abstract: Neutral sugar analysis was applied to wood meal taken from various sapwood positions in the tension wood stem of yellow poplar (*Liriodendron tulipifera*), and the results were compared with those of lignin analyses previously reported. The yield of glucose was higher along the periphery of the stem toward the tension wood part. In contrast, the yields of xylose and mannose were lower in this direction. A high positive correlation was observed between mannose yield and Klason lignin content ($R^2 = 0.92$). The xylose yield was also correlated with the methoxyl content of the Klason residue ($R^2 = 0.93$) and the *erythro*/*threo* ratio of β-O-4 structures ($R^2 = 0.95$).

Keywords: reaction wood, mannan, xylan, lignin content, arylglycerol-β-aryl ether

2012-P12

深海沈木から単離したバクテリアの分類学的位置と芳香族モノマー代謝

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Phylogenetic analysis of culturable bacteria from deep-sea sunken wood and their aromatic compounds metabolism

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Abstract: Functional screenings of culturable bacteria isolated from sunken wood collected from the deep sea revealed the existence of capable of metabolizing lignin-related aromatic compounds. The isolates were classified into diverse phyla, including Firmicutes, Actinobacteria, Bacteroidetes, and Proteobacteria. Twenty-one unique 16S rRNA gene sequences were detected including marine lineage isolates. The metabolites of the isolates were analyzed using liquid chromatography/mass spectrometry (LC/MS) or gas chromatography/mass spectrometry (GC/MS). Most of the representative isolates non-oxidatively decarboxylated the substrates to produce the corresponding aromatic vinyl monomers, which are used as feed stocks for bio-based plastics production. Oxidative metabolism of the lignin-related compounds for assimilation was frequently observed. Our study showed that the deep-sea environment contains an abundance of microorganisms capable of both non-oxidative and oxidative bioconversion of lignin-derived aromatic compounds. The ability for bioconversion of aromatic compounds found in this study will facilitate the development of future biotechnological applications.

Keywords: aromatic compounds, bioconversion, deep-sea bacteria, phenolic acid, vinyl monomer

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2013-101

イネ *brown-midrib* 変異体の解析

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Characterization of *brown-midrib* mutant in rice plant

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Abstract: Several *brown midrib* (*bm*) mutants have so far been isolated from the C4 grasses, maize, sorghum and pearl millet, but have not been detected in C3 grasses including rice (*Oryza sativa*). In the present study we characterized the *cad2* (*cinnamyl alcohol dehydrogenase 2*) null mutant isolated from retrotransposon *Tos17* insertion lines of *Oryza sativa* L. ssp. *japonica* cv. Nipponbare. This mutant exhibited brown-colored midribs in addition to hulls and internodes, clearly indicating both *bm* and *gold hull and internode* (*gh*) phenotypes. The enzymatic saccharification efficiency in the culm of cad2 null mutant was increased by 16.1% than that of the control plants. The lignin content of the *cad2* null mutant was 14.6% lower than that of the control plants. Thioacidolysis of the *cad2* null mutant indicated the presence of cinnamaldehyde structures in the lignin. Taken together, our results show that deficiency of *OsCAD2* causes the *bm* phenotype in addition to *gh*, and that the coloration is probably due to the accumulation of cinnamaldehyde-related structures in the lignin. Additionally, this *cad2* null mutant was useful to silage purposes and biofuel production.

Keywords: lignin, rice, cinnamyl alcohol dehydrogenase, *brown midrib*, mutant

2013-102

リグニン・多糖複合体分解酵素の植物体での発現

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Expression of lignin-carbohydrate complex degrading enzyme in the plant

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Abstract: We aim to increase the industrial values of crops by improvement of the digestibility of the forage crop and conversion rate to saccharification from biomass. We have been challenging to modify the lignin content and structures, by suppression of the genes for the lignin biosynthetic pathway or expression of lignin degradation enzymes. In this research, we tried to reduce the linkages between lignin and carbohydrate by introduction of a lignin-carbohydrate-complex decomposition enzyme gene to tobacco plants. CcEST1 is an esterase of a white-rot-fungus, *Coprinopsis cinerea*. This enzyme can decompose bonds between the lignin and polysaccharide. CcEST1 has feruloylesterase activity and acetyltransesterase activity. We altered the gene to effectively secrete to the plant extracellular space and induced to tobacco plants. The esterase activities of the transformed plants were higher than that of the wild type plant.

Keywords: lignin, *Nicotiana tabacum*, *Coprinopsis cinerea*, esterase, *Agrabacterium tumefaciens*, degrading enzyme, lignocarbohydrate complex, *prxA3a*

2013-103

リグニンを高分子化する植物ペルオキシダーゼの酸化能

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Oxidation ability of plant peroxidases contributing to lignin formation

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Abstract: The final step of lignin biosynthesis, which is catalyzed by a plant peroxidase, is the oxidative coupling of the monolignols to growing lignin polymers. Cationic cell-wall-bound peroxidase (CWPO-C) from poplar callus is a unique enzyme that has oxidative activity for both monolignols and synthetic lignin polymers. We previously identified that three putative CWPO-C homologues (AtPrx2, AtPrx25 and AtPrx71) were related to lignin biosynthesis in Arabidopsis by the analysis of the knockout mutants. In this study, we showed that recombinant proteins of AtPrx2, AtPrx25 and AtPrx71 have high oxidation activity for syringyl compound. Moreover, assays with ferrocytochrome *c* showed that AtPrx2, AtPrx25 and AtPrx71 had high molecular compound oxidation activity unlike AtPrx53 that is representative plant peroxidase. These results suggest that such a property which can oxidize syringyl compounds and high molecular compounds is indispensable as a lignin polymerization enzyme in vascular plants.

Keywords: plant peroxidase, lignin polymerization, *Arabidopsis thaliana*

2013-104

リグニンの形成過程に関する研究

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Studies on formation process of lignin

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Abstract: After the dehydrogenative polymerization of coniferyl alcohol and its dimer model compounds (β-O-4, β-5, and β-β) using horseradish peroxidase, we analyzed the time courses of substrate amounts and the reaction products by LC-MS/MS. The consumption rate of coniferyl alcohol was far higher than that of the dimers and there were difference among the consumption rates of the three dimers. From the results of cyclic voltammogram, the consumption rate was not correlated with the radical oxidation potential. There were some differences on the consumption rates of the dimers between in the sole system and mixed system. We detected that coniferyl alcohol tetramers, hexamers, and octamers were formed during the polymerization reaction of the dimers. It was confirmed that major bonding patterns between the dimers were 5-5´ and 4-O-5´ by analysis of dehydrogenative polymerization products of [5-D] coniferyl alcohol dimers.

Keywords: monolignol, oligolignol, radical coupling, reaction rate, bonding type

2013-105

^{13}C 標識法を用いたイネリグニンの構造解析

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Structural analysis of rice plant lignin by ^{13}C-enrichment technique

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Abstract: In order to analyze lignin structures, a technique have been developed using specific ^{13}C-enrichment of the C$_{\alpha}$ of the phenylpropanoid unit by feeding coniferin-[α-^{13}C] and syringin -[α-^{13}C] to rice plant. After milling of the extractive-free sample followed by acetylation for dissolving the sample in $CDCl_3$, high-resolution two dimensional (2D) ^{13}C-^{1}H correlation HSQC (hetero-nuclear single quantum coherence) spectrum of the whole cell wall material was recorded in the solution-state. Making difference NMR spectrum between the ^{13}C-enriched lignin and unenriched lignin provided a simple spectrum arising exclusively from the ^{13}C-enriched carbons. From the simplified difference HSQC spectrum, quantitative determination was made on the frequencies of major inter-unit bonds involving C$_{\alpha}$. To investigate the incorporation of the ^{13}C-enriched monolignol administrated as monolignol glucosides, stable carbon isotope compositions on the rice plant stems and leaves were determined by measuring δ^{13}C.

Keywords: lignin, rice plant , ^{13}C-enrichment, High-Resolution NMR, δ^{13}C

2013-106

スピロジエノン構造に関する研究：同モデル化合物の酸処理によるジアリールプロパン構造の生成

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Study on spirodienone structures in lignin: the formation of diarylpropane structure from spiriodienone model compound by acid treatment

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Abstract: A model compound for spirodienone structures in lignin was treated with acetic acid or hydrochloric acid at room temperature (27ºC). While the model compound was stable in deuteroacetic acid (CD_3COOD), it disappeared within 3 hours by 0.1M duterochloric acid (DCl) treatment in dioxane-water (dioxane-*d8*:D_2O, 80:20, v/v). As an acidolysis product, a diarylpropane was formed in over 80% yield.

Keywords: β-1 linkage, spirodienone, diarylpropane, acidolysis, NMR,

2013-107

Eucalyptus globulus MWL 抽出残渣中の phenyl glycoside 型 LCC の構造解析

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Structural analysis of phenyl glycoside type LCC of *Eucalyptus globulus* in residues left after MWL isolation

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Abstract: Several monolignol glycosides, including coniferyl alcohol, sinapyl alcohol and *p*-coumaryl alcohol, bearing different sugar moieties were synthesized to obtain fundamental NMR data for the structural analysis of phenyl glycoside type lignin-carbohydrate complex (LCC). The correlations observed for the $C_{1\beta}$-$H_{1\beta}$ bonds of the sugar moieties in the HSQC spectra of the monolignol β-glycosides varied and were in the range of δ_C/δ_H 97-105/4.7-5.2 ppm. The correlations of syringin and the sinapyl alcohol β-xyloside appeared in the neighborhood of that of phenyl glycoside type lignin-carbohydrate (LC) linkage in the HSQC NMR spectrum of the fraction from the residues of *Eucalyptus globulus* left after MWL isolation. Suggesting that phenyl glycoside type LC linkages in the residues might be the glycosidic bonds between syringyl lignin and cellulose or xylan.

Keywords: lignin-carbohydrate complex (LCC), phenyl glycoside, monolignol glycoside, HSQC NMR, *Eucalyptus globulus*

2013-108

リグニン β-O-4 結合新規選択的開裂法(γ-TTSA 法)(6)-粗 MWL 分解物の分画および構造解析-

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Studies on the selective cleavage method for β-O-4 linkages of lignins (γ-TTSA method)(6) – the fractionation and the structure analysis of the degradation products of crude MWL by γ-TTSA method –

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Abstract: The γ-TTSA method (consisted of four reactions; tosylation, thioetherification, sulfonation, alkali-treatment), which has been proposed as new selective β-O-4 cleavage method, was applied to crude Milled Wood Lignin (cMWL1) from *Eucalyptus globulus*. As a consequence, the lignin in the cMWL1 was selectively degraded as expected, to get the degradation product (cMWL5). The cMWL5 was further fractionated with the extraction of Et_2O, EtOAc, THF to get the four fractions (cMWL5-1~ cMWL5-4). HSQC-NMR spectra of the four degradation products suggested that cMWL5-1 consists low molecular lignin degradation products and cMWL5-2~cMWL5-4 were new LCC fractions. Especially, cMWL5-4 is an interesting LCC fraction in that xylan accounts for a large percentage differently from the others.

Keywords: crude MWL, γ-TTSA method, LCC, selective cleavage of β-O-4 linkage

2013-109

緑液前処理条件下における *β-O*-4 型非フェノール性リグニンモデル化合物の反応

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Reaction of nonphenolic *β-O*-4 type lignin model compound under green liquor pretreatment conditions

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Abstract: Green liquor (GL, from Kraft pulp mill) pretreatment showed a great potential in efficient and selective removal of lignin from lignocellulose. The mechanisms of delignification in GL pretreatment should need to be investigated. In this study, a nonphenolic *β-O*-4 type lignin model compound was synthesized and cooked with various liquors including GL to investigate the reactions of nonphenolic *β-O*-4 lignin moiety under GL pretreatment conditions. The results showed that the nonphenolic *β-O*-4 bond of VG is broken under the GL cooking conditions. Either of the Na_2CO_3 or NaSH solution caused the cleavage of *β-O*-4 bond only slowly, although the former solution resulted in the disappearance of VG more rapidly than the latter. The Na_2CO_3 solution mixed with NaSH not only enhanced the *β-O*-4 bond cleavage significantly but also changed reaction products obtained, showing that reactions occurred in this mixed solution are different from those in the Na_2CO_3 or NaSH solution. These results suggest that there is a synergistic effect between CO_3^{2-} and HS^- on the *β-O*-4 bond cleavage during GL cooking, although the reaction mechanism is not clear.

Keywords: Alkali, Carbonate, Green liquor, Hydrosulfide, Pulping

2013-110

半流通型加圧熱水処理によるスギリグニン分解物の MALDI-TOF/MS 分析

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MALDI-TOF/MS analysis of lignin-derived products from Japanese cedar as treated by semi-flow hot-compressed water

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Abstract: By MALDI-TOF/MS analysis of lignin-derived products from Japanese cedar (*Cryptomeria japonica*) as treated by semi-flow hot-compressed water (230℃/10MPa/15min), the decomposition behavior of lignin was discussed. As a result, several molecular weight intervals of 178 were observed in fractions collected during the increasing temperature up to 230℃, whereas more molecular weight intervals of 196 were in fractions under constant temperature of 230℃. The former interval of 178 may be derived from β-β or β-5 linkage, while the latter 196 from β-O-4 linkage. Therefore, during the increasing temperatures, the lignin-derived products in water-soluble portion would be more composed of condensed type linkages, whereas those during the constant temperature more of ether type linkages. From these lines of evidence, it was speculated that, during the increasing temperatures, condensed type-rich lignin-derived products were eluted in hot-compressed water due to the cleavage of ether linkage, whereas after reaching at 230℃, some micropores have occurred in the cell wall due to hemicellulose decomposition during the increasing temperature, some clusters of the rather large lignin molecules were eluted, and its lignin structure must be originated from the natural lignin itself, thus more of the ether type of linkages of lignin. These results indicate that MALDI-TOF/MS is a powerful tool for analysis of lignin-derived products.

Keywords: water-soluble lignin, bulk delignification, GC-MS, DFRC method, condensed type lignin

2013-111

側鎖からの水素引抜によるリグニンの熱分解ラジカル連鎖 β-エーテル開裂機構の検討

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Lignin radical chain β-ether-cleavage reactions through Abstraction of hydrogen from the side chain

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Abstract: Pyrolytic radical chain cleavage mechanisms of lignin-β-ether linkages were studied with the β-ether type lignin model dimers which were deuterated at the Cα-, Cβ- and Cγ- positions, respevtively. The isotope effects on their reactivities were studied under the pyrolysis conditions (N_2/350℃/2min in the presence of Japanese ceder wood as a radical source). The reactivitiy was not reduced by deuteration at the Cα- or Cβ-position. On the other hand, the reactivity of the Cγ- deuterated dimer decreased significantly. Since the bond dissociation energy (BDE) of the Cγ-H bond are rather higher than that of Cα-H bond, these results suggest that the accessibility of radicals to the hydrogen atom is more important than the BDE of C-H bond. This proposal is supported by the stereoelectronic factor required for the hydrogen Abstraction; liner interaction between radical and H-C bond is required. Formation mechanisms of the Cα=Cβ and vinyl ether/ Cβ･･･types of products are also discussed based on the deuterium retention in these products, which were measured with their ^{1}H NMR analysis. The Cα=Cβ type product is suggested to be formed through Abstraction of hydrogen from the Cγ. As for vinyl ether and its hydrolysis product (Cβ･･･type product), it was found that the deuterium retention data are not adequate for determination of their formation mechanisms, since the keto-enol ether-type tautomerization occurring during pyrolysis would eliminate the deuterium atom from the Cα- and Cγ- positions.

Keywords: radical chain reaction, pyrolysis, ether cleavage, deuteration, isotope effect

2013-112

工業リグニンを原料とするポリカプロラクトン誘導体の合成と熱的性質

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Preparation and thermal properties of industrial lignin based polycaprolactone derivatives

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Abstract: Based on two kinds of industrial lignin, such as hydrolysis (HL) and sodium lignosufonate (LS), polycaprolactone (PCL) derivatives were prepared via ring opening polymerization using hydroxyl group of lignin as a reaction site. By controlling the mass of □-caprolactone, molecular mass of PCL side chain was varied from 1.1x10^3 to 1.1x10^4. Conversion rate of polymerization was ca. 100 %. Thermal properties of the lignin-PCL polymers were measured by differential scanning calorimetry and thermogravimetry. Mechanical tests were also carried out. Glass transition was observed at around -70 to -60 °C and melting temperature was found at around 50 °C depending on molecular mass of PCL. Crystallinity calculated from enthalpy of melting was 37-42%. Decomposition temperature was 370 to 400 °C. Breaking strength increased with increasing molecular mass of PCL.

Keywords: hydrolysis lignin, sodium lignosulfonate, □-caprolactone, glass transition, melting temperature

2013-特別講演、

リグニン研究から始まった環境に優しい高圧水蒸気による森林資源の総合利用技術-- 爆砕処理、圧縮成形加工、3 次元深絞り加工、バインダーレスバード、高圧水蒸気蒸留 –

棚橋 光彦
飛騨産業株式会社 キツツキ森の研究所

2013- Invited lecture:

Total utilization technique of forest resources by ecop process with high-pressure steam beginning from research for lignins – Steam explosion, compression molding, three dimensional deep-drawing, binderless-boads, high-pressure steam-distraction

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Abstract: Starting from lignin chemistry such as synthesis of lignin model compounds, elucidation of chemical structure of lignin and dehydrogenative polymerization of monolignols, eco-friendly total utilization wood techniques using high pressure steam were developed. I had researched the reaction mechanism of wood components and the separation of main degradation products from wood and these effective utilization such as bioethanol and cattle feed from woods by steam explosion technique. In this study, I found that cellulose crystalline structure transformed from Ⅰαto Ⅰβ by high-pressure steam-treatment. Taking advantage of this finding, the compressive molding method with high-pressure steam has been developed in our laboratory, as an ecological method to make products from sawdust, leaves and branches, which arise from wood-based industries as waste. By this method, logs can be transformed into squares, and sawdust, leaves or branches into biomass boards. Square timber will widely be used as building materials, and biomass board to be used for weed suppressers or spreading materials on the sidewalk. For example, the board made by this method already has been used at many places, e.g., walking paths in Kenrokuen Garden. In addition, much essential oil mainly terpenoids can also be obtained through this process. It was found that the essential oil contained furfural and 5-hydroxymethyl-2-furfural, which are byproducts from saccharides and hemicelluloses with high temperature steaming. Furthermore a new apparatus was developed by combining a high pressure distillator with the compressive molding apparatus. With this apparatus, the distillation of higher boiling compounds such as sesqui-terpenoids and di-terpenoids, linans such as magnolol and sesamine and some degradation producte from lignin such as syringaresinols which are hardly distilled with 100 ºC steam was made possible. In the case of operations at several saturated steam pressures (0.4-1.6 MPa) for 60 min, the yields of these compounds increased with steam pressure within the limits of this experiment.

Keywords: high-pressure steam treatment, transformation of cellulose Iα to Iβ, compression molding, permanent fixation, flexible wood, high-pressure steam-distillation

2013-201

針葉樹アルカリ蒸解黒液粉末のPEG処理による炭素繊維原料用リグニン誘導体

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Lignin derivatives by alkaline-PEG treatment of softwood black liquor powder for preparing carbon fiber precursor

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Abstract: Thermal melt spinning is a major industrial process to produce commercial carbon fiber precursor. To prepare lignin based carbon fiber precursor following the commercial process, lignin should melt in heating without bringing thermo degradation. It is reported that some hardwood lignin melts at elevated temperature, however, softwood lignin such as softwood soda-anthraquinone (AQ) lignin does not show thermal melting property. To prepare softwood lignin based carbon fiber, lignin should be modified to improve its thermal properties. We found a new simple process to prepare lignin derivatives that have adequate thermal melting property. In the process, black liquor powder was directly modified by PEGs in alkaline condition. In this paper, the properties of the alkaline PEG treated lignin were discussed.

Keywords: carbon fiber, PEG, softwood lignin, softening temperature, dried black liquor powder

2013-202

オルガノソルブリグニンを原料とする電気二重層キャパシタ用電極の調製

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Preparation of electrode for electric double layer capacitor from organosolv lignin

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Abstract: An electric double layer capacitor (EDLC) was successfully prepared from electrospun organosolv lignin fibers. This preparation was carried out by the following process. The electrospun fibers were converted to activated carbon fibers (ACFs) by thermostabilization followed by carbonization and steam activation. The ACFs were suspended together with conductive carbon black (5%) in aqueous carboxymethyl-cellulose solution, and then this suspension was spread on a thin Al foil. The foil and paper as a separator was immersed in triethylmethylammonium tetrafluoroborate/ propylene carbonate solution as an organic electrolyte. Finally, these materials were assembled in a measurement cell. This EDLC showed electrostatic capacitance of 142 F/g and impedance of 12 □.

Keywords: electric double layer capacitor (EDLC), electrospinning, electrode, acetic acid lignin (AL), carbon fibers (CFs)

2013-203

両親媒性サゴヤシリグニンを用いたサゴヤシ廃棄物の酵素糖化

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Enzymatic saccharification of sago palm waste with amphipathic sago-lignin derivatives

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Abstract: The effect of amphipathic sago-lignin derivatives as a cellulase-aid agent on enzymatic saccharification of pulps from sago palm waste, disposed after starch extraction, was evaluated, in terms of saccharification efficiency and remaining cellulase activity. This saccharification was repeated (1st to 4th run), using cellulase purified by ultrafiltration after each run. Without additive, glucose yield was dramatically decreased by repeated use of cellulase. However, it was found that glucose yield and cellulase activity maintained at a higher level by the addition of the amphipathic lignin derivatives.

Keywords: sago palm waste, saccharification, cellulolytic enzyme, critical micelle concentration, hydrophobic interaction

2013-204

酸素漂白過程における炭水化物の被攻撃部位の特定

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Specification of carbohydrate substructure attacked by active oxygen species in oxygen bleaching process

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Abstract: In this study, a clear kinetic isotope effect was observed when a pair of carbohydrate model compounds, methyl β-D-glucopyranoside (MGP) and its deuterated compound at the C-3 or C-4 position, methyl β-D-(3-^{2}H)glucopyranoside or methyl β-D-(4-^{2}H)glucopyranoside, respectively, was reacted with active oxygen species (AOS) generated by reactions of O_2 with a phenolic compound, 2,4,6-trimethylphenol (TMPh), under oxygen bleaching conditions. However, no clear kinetic isotope effect was observed when a pair of MGP and its deuterated compound labeled at the C-5 or C-6 position, methyl β-D-(5-^{2}H)glucopyranoside or methyl β-D-(6,6'-^{2}H)glucopyranoside, respectively, was reacted with the AOS under the oxygen bleaching conditions. These results may suggest that the AOS **Abstract** the C-3 and C-4 hydrogens more frequently than they **Abstract** the C-5 and C-6 hydrogens. It may further be suggested that the C-2 hydrogen is **Abstract**ed by the AOS more easily than the other hydrogens.

Keyword: cellulose, pulp, active oxygen species, lignin, oxygen delignification

2013-205

アブラヤシ空果房の効率的糖化のための前処理への蒸解漂白法の適用

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Application of pulping and bleaching method to pretreatment of empty fruit bunch for effective enzymatic saccharification

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Abstract: This study aimed to develop pretreatment process of oil palm empty fruit bunch (EFB) for effective enzymatic saccharification by applying wood cooking and pulp bleaching method. Firstly, EFB fibers were subjected to prehydrolysis/ soda-anthraquinone (AQ) cooking and prehydrolysis/ acid sulfite cooking, and subsequently oxygen bleaching to compare the lignin contents and pulp yields between of EFB pulps prepared by different cooking methods. Secondly, the enzymatic saccharification rates of EFB pulps prepared by prehydrolysis/ acid sulfite and prehydrolysis/ soda-AQ cookings were compared. By enzymatic saccharification, the amount of glucose liberated from acid sulfite pulp was lower than that of soda-AQ pulp. However, the oxygen bleaching treatment significantly increased the glucose liberation by enzyme from EFB acid sulfite pulp.

Keywords: pretreatment, delignification, soda-AQ cooking, acid sulfite cooking, enzymatic saccharification

2013-206

針葉樹材からのセルロース精製および酵素糖化前処理としての 1-ethyl-3-methylimidazolium acetate 処理法の検討

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Treatment with 1-ethyl-3-methylimidazolium acetate as refining method of cellulose from softwood and pre-treatment for enzymatic saccharification

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Abstractionic liquid treatment with 1-ethyl-3-methylimidazolium acetate ([Emim]Ac) was studied as cellulose production method and pre-treatment for enzymatic saccharification of Japanese softwood. A part of cellulose, hemicellulose and lignin in wood were dissolved by [Emim]Ac treatment from wood meals of *Cryptomeria Japonica*. After dissolution, some parts of these components were collected as regenerated cellulose and the other parts remain dissolved as oligomer in filtrate. The regenerated cellulose and [Emim]Ac treated wood sample which collected as residue contained [Emim]Ac even after washing with dimethyl sulfoxide. The yield of glucose liberated from regenerated cellulose by enzymatic saccharification was higher than that of filter paper. The residue contained lignin little less than non-treated wood sample, however the glucose yield was 51.1% and it was much higher than that of non-treated wood sample. Moreover, the yield of glucose liberated from residue was increased to 90.1% after decreasing the amount of contained [Emim]Ac from 25.1% to 3.9% by washing with water. These results indicated that [Emim]Ac treated samples can be applied to enzymatic saccharification without separating regenerated cellulose and residue.

Keywords: 1-ethyl-3-methylimidazolium acetate, enzymatic saccharification, *Cryptomeria Japonica*, Py-GC/MS

2013-207

ESI-FT-ICR MS によるリグノセルロース骨格構造モデルとセルラーゼとの複合体形成解析

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Analysis of complex formation between lignocellulose model compounds and cellulase by ESI-FT-ICR MS

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Abstract: In enzymatic hydrolysis of woody biomass by cellulase, inhibition of hydrolytic activity by adsorption between insoluble lignocellulose and cellulase has been widely known, but interaction between low molecular mass lignin degradation products and cellulolytic enzymes are not well understood. We analysed adsorption of cellulase on lignin dimer model compounds or cellooligosaccharides by ultra-high resolution mass spectrometry. Complex formation of endoglucanase or *Cj*CBM28 with lignin dimer model compounds was observed as well as that with cellooligosaccharides. Not only stoichiometric but also multiple intermolecular interactions between cellulase component and lignin model compounds were demonstrated by the mass spectra.

Keywords: cellulase, inhibitor, ligninocellulose, complex formation, ESI-FT-ICR MS

2013-208

ピルビン酸デカルボキシラーゼ遺伝子高発現による白色腐朽菌におけるアルコール発酵能改善

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Improvement of alcohol fermentation ability by overexpression of pyruvate decarboxylase gene in white-rot-fungi

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Abstract: To produce ethanol effectively from woody biomass by hyper lignin-degrading fungus *Phanerochaete sordida* YK-624, the gene of pyruvate decarboxylase (*pdc*) which is a key enzyme in alcohol fermentation, was cloned. The promoter of glyceraldehyde-3-phosphate dehydrogenase gene cloned from *P. sordida* YK-624 was used to drive the expression of *pdc*. The expression vector was transformed into a *P. sordida* YK-624 uracil auxotrophic mutant, UV-64. Thirteen of 16 transforamants showed higher production of ethanol than wild type. The strain GP7, which showed the highest production of ethanol among all transformants, indicated higher PDC activity and transcription of *pdc*. These results suggest that the overexpression of *pdc* is effective for the improvement of alcohol fermentation in white-rot fungi.

Keywords: white-rot fungi, molecular breeding, pyruvate decarboxylase, alcohol fermentation, *Phanerochaete sordida* YK-624

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非フェノール性リグニンモデル化合物の分解を触媒するカワラタケ培養物由来のラッカーゼメディエーター

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Degradation of a nonphenolic lignin model compound catalyzed by laccase in the presence of mediators isolated from the cultures of *Trametes versicolor*

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Abstract: Laccase (EC 1.10.3.2) is widely found in white-rot fungi and catalyzes one-electron oxidation of phenolic substances to form many oxidation products *via* phenoxy radicals. In the presence of appropriate compounds (mediators), laccase degrades nonphenolic lignin model compounds that are resistant to degradation by laccase alone. has been reported. However, there are few report for the identification of natural laccase mediators.

In this report, we searched the natural laccase mediators in the extacellular culture fluid of *Trametes versicolor* for laccase production and in the whole-culture pf beech wood incubated with *T. versicolor*. The results indicated that laccase in the presence of the low molecular phenols isolated from these cultures of *T. versicolor* could catalyzed the degradation of a nonphenolic β-*O*-4 lignin model dimer *via* the Cα-oxidation, β-ether cleavage and aromatic ring cleavage. The degradation mechanisms are very similar to those for laccase/1-hydroybenzotriazole system and lignin peroxidase.

Keyword: laccase, natural mediator, *p*-hydroxybenzoic acid, vanyllyl alcohol, nonphenolic β-*O*-4 lignin model dimer,

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高活性リグニン分解菌 *Phanerochaete sordida* YK-624 株によるビスフェノール A の分解機構の解明

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Metabolism of bisphenol A by hyper lignin-degrading fungus *Phanerochaete sordida* YK-624

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Abstract: A (BPA) is one of the representative compounds of the endocrine disrupting compounds group and the highest volume chemicals produced worldwide. As a result, BPA is often detected in many soil and water environments. We demonstrated the metabolism of BPA from liquid cultures inoculated with hyper lignin-degrading fungus *Phanerochaete sordida* YK-624. Both ligninolytic and non-ligninolytic condition, BPA were effectively decreased and metabolites were detected by ESI-MS and NMR analysis. Under the ligninolytic condition, BPA is oxidized to BPA phenoxy radicals by ligninolytic enzymes and then dimerized at extracellular region. On the other hand, BPA is firstly monooxygenated to hydroxy-BPA by cytochrome P450, and then methylated by *P. sordida* YK-624 under the non-ligninolytic condition.

Keywords: *Phanerochaete sordida* YK-624; bsphenol A; estrogenic activity; metabolic pathway

2013-211

Aliphatic biotransformation and crude oil biodegradation by *Pestalotiopsis* sp.

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Abstract: In this study, the ability of *Pestalotiopsis* sp. NG007 to degrade and transform aliphatic mixture and its importance to biodegradation of crude oils was investigated in liquid medium. During the biodegradation of an aliphatic mixture (*n*-decane, *n*-undecane, *n*-dodecane, *n*-tetradecane, *n*-pentadecane, *n*-hexadecane, *n*-octadecane, *n*-nonadecane, *n*-eicosane and pristane), fifteen metabolites were detected. The presence of fatty alcohols, fatty aldehydes, and fatty acids (mono- and di-carboxylic acid) as intermediate products showed that NG007 can degrade and transform aliphatic fractions not only via mono- or di-terminal oxidation, but also via sub-terminal and alkyl peroxide oxidation. In co-culture with *Polyporu*s sp. S133 (basidiomycetes fungus), the enhancement of crude oil biodegradation occurred via accelerated biodegradation of aliphatic and aromatic fraction. Addition of piperonyl butoxide or $AgNO_3$ inhibited biodegradation by 81-99%, which revealed the important role of P450 monoxygenases and/or dioxygenases in the initial degradation of the aliphatic and aromatic fractions in petroleum hydrocarbons.

Keywords: aliphatic, biodegradation, crude oil, monooxygenase, *Pestalotiopsis* sp.

2013-P01

特異的な広葉樹あて材形成とリグニン分布の関係

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Relationship between specific reaction wood formation and lignin distribution in angiosperms

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Abstract: Lignin distribution of reaction woods in *Sarcandra glabra* and *Gardenia jasminoides* were investigated to clarify the relationship between specific reaction wood formation and lignin distribution in angiosperm species. Based on the results of absorbance measured by visible-light microspectroscopy after Wiesner and Mäule color reactions in normal wood, secondary wall of tracheid in *S. glabra* and wood fiber in *G. jasminoides* were suggested to be mainly composed of guaiacyl lignin, and both guaiacyl and syringyl lignin, respectively. On the lower side of inclined stems in both species, increase in guaiacyl lignin was found compared with normal wood and upper side of inclined stems. Based on the results, it is considered that increase in guaiacyl lignin may be an important factor for the species which form reaction wood on the lower side of inclined stems in angiosperms.

Keywords: vessel-less angiosperms, Wiesner color reaction, Mäule color reaction, reaction wood

2013-P02

カバノアナタケ菌 IO-U1 株に感染したシラカンバ幼植物体 No.8 に発現するペルオキシダーゼの MALDI/TOF/MS イメージング

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MALDI/TOF/MS imaging analysis of peroxidase expressed specifically in the Japanese birch plantlet No.8 infected with *Inonotus obliquus* strain IO-U1

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Abstract: The present study aimed at clarifying the roles of the peroxidases, which were specifically expressed in the Japanese birch plantlet No.8 infected with *Inonotus obliquus* strain IO-U1, in the basic resistance mechanisms of the plantlet against the fungus. The specific peroxidases expressed by the fungal infection were isolated by isoelectric focusing and analyzed by MALDI/TOF/MS. The distribution of the specific peroxidases in the plantlet was investigated by using the obtained mass spectra and MALDI/TOF/MS imaging. The obtained results indicated that the peroxidases expressed specifically by injury and fungal infection distribute mostly in xylem, especially the peroxidases by fungal infection distribute in the specific part of xylem.

Keywords: basal resistance, canker-rot fungus, isozyme, mass spectrometry, tree pathology

2013-P03

セルロースミクロフィブリルゲルを用いた人工木化の試み

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Cellulose microfibril-based scaffold for artificial lignification

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Abstract: The aim of the present study was to evaluate a cellulose microfibril based-hydrogel as a scaffold for artificial lignification. The cellulose microfibril aggregates isolated from softwood had a uniform width of approx. 15 nm and lengths over several micrometers. The hydrogel was prepared from the microfibril suspension through sodium hydroxide treatment and it had a layered structure of microfibril network and its appearance was essentially the same as that of the primary wall of wood cells before lignification. We attempted to synthesize DHPs on the surface and inside of the gel a by step-by-step reaction of the gel saturated with coniferyl alcohol and horseradish peroxidase in a H_2O_2 solution. As the lignification step was repeated, the color of the gels gradually changed from translucent white to light brownish white and the volume was increased with the increase in the number of polymerization times. This study confirmed that it is possible to deposit DHP lignins in cellulose microfibril-based gels.

Keywords: lignification; cellulose microfibril; scaffold; hydrogel

2013-P04

β-*O*-4 型オリゴリグノールの合成研究

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Synthetic study on *β–O*-4 type oligolignols

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Abstract: Artificial lignin polymers with *β-O*-4 linkages have been synthesized in our laboratory. In this study two synthetic strategies: convergent and linear syntheses were evaluated for the synthesis of *β-O*-4 type oligolignols with distinct degree of polymerization. A key reaction step was Williamson ether formation, which includes nucleophilic substitution under basic conditions. Effect of several bases and protective groups were investigated and a trimer was synthesized by the linear synthetic strategy.

Keywords: oligomeric model compound, dimer, tetramer, oligomer

2013-P05

β-*O*-4 構造を有する phenyl glycoside 型 LCC モデル化合物の合成

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Synthesis of dilignol β-glycosides with β-*O*-4 structures

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Abstract: To get fundamental HSQC NMR data for phenyl glycoside type LCC analyses, the syntheses of dilignol β-glycosides having β-*O*-4 structure which is the most common structure in lignin were performed. Guaiacylglycerol-β-guaiacyl ether (**1G*e***) was per-acetylated with Ac_2O / pyridine to give compound **2G*e*** (99.7%). The compound was treated with hydrazine in THF to afford compound **3G*e*** (74.0%). The glycosylation of compound **3G*e*** with compound **4** in the presence of BF_3-Et_2O in dry CH_2Cl_2 afforded only β-glycoside **6G*e*** (97.3%). Deacylation of compound **6G*e*** with NaOMe / MeOH gave target material **8G*e*** (72.3%). The synthetic method for compound **8G*e*** was applied to the syntheses of other β-glycosides. The correlations derived from $C_{1\beta}$-$H_{1\beta}$ of sugar moieties of β-glycosides are different from existing ones and present in the region approx. δ_C / δ_H 100-104 / 4.8-4.9 ppm where supposedly signals derived from phenyl glycoside LC linkage would appear.

Keywords: lignin-carbohydrate complex (LCC), 2D-NMR, phenyl glycoside, dilignol β-glycoside, β-O-4 structure

2013-P06

TEMPOによるリグニンの電解酸化の検討

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TEMPO-mediated electro-oxidation of lignin model compounds

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Abstract: The TEMPO and its derivatives-mediated electro-oxidation of lignin were investigated. The electrolysis of dimeric lignin model compound **1G** (4-ethoxy-3-methoxyphenylgltcerol-β-guaiacyl ether) in acetonitrile-water afforded the corresponding Cα-carbonyl compound **2G**. On the other hand, the electro oxidation of **1G** with TEMPO in 10% dioxane-buffer afforded the corresponding Cγ-carboxyl compound **3G** in high yield. In both systems, the yields of the oxidative products by the electrolysis with 4-acetoamide-TEMPO were higher than those with TEMPO.

Keyword: 2,2,6,6-tetramethylpiperidine-*N*-oxyl, 4-AcNH-TEMPO, electrolysis, mediator, lignin

2013-P07

エレクトロスピニング法によるリグニン／セルロースナノクリスタル複合ナノファイバー合成と炭素化の検討

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Electrospun lignin based nanofibers reinforced with cellulose nanocrystal and carbonization

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Abstract: Lignin-based fibers were produced by electrospinning aqueous dispersions of lignin, poly(vinyl alcohol) (PVA), and cellulose nanocrystals (CNC's). Dispersion properties including viscosity, electrical conductivity, and surface tension were examined and correlated to the electro-spinnability and resulting morphology of the composite fibers. The influence of CNC's on the thermal properties of the multi-component materials was investigated by using thermal gravimetric analysisand differential scanning calorimetry The thermal stability of the system was observed to increase owing to a strong interaction of the lignin-PVA matrix with the dispersed CNCs, mainly via hydrogen bonding as observed in Fourier transform infrared spectroscopy experiments. Heat treatment on the lignin electrospun fibers was carried out by using of nitrogen atmosphere at various temperatures, followed by carbonization at 1000 °C. Carbonized fibers were evaluated using SEM, WAXD, and Raman spectroscopy.

Keywords: electrpspinning, cellulose nanocrystal, composite, thermal mechanical property, carbon fiber

2013-P08

リグニンおよびテルペン由来成分を原料とするエステル系エポキシ樹脂の合成と熱的性質

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Synthesis and thermal properties of epoxy resins derived from lignin and terpene-based component

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Abstract: Epoxy resins were prepared using alcoholysis lignin (AL) and terpene-based component. AL was dissolved in the same amount of glycerol (GLY). The obtained solution was allowed to react with succinic anhydride in order to synthesize the mixture ester-acid derivatives of AL and glycerol (ALGLYPA). A ester-acid derivative of GLY (GLYPA) was synthesized from GLY. When the obtained ALGLYPA and GLYPA were allowed to react with 1,3-bis(3,4-epoxycyclohexenyl9-p-menthane (BECHM), the weight contents of ALGLYPA $\{W_{ALGLYPA}/(W_{ALGLYPA}+W_{GLYPA})\}$ were change from 0 to 100 %. [EPOXY]/[ACID] mole ratio was maintained at 1.0. Thermal properties of the obtained cured epoxy resins were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG). The glass transition temperatures (T_g's) increased and reached a constant value when ALGLYPA contents were increased. The thermal decomposition temperatures (T_d's) and mass residues at 500 °C were almost constant regardless of ALGLYPA contents.

Keywords:l ignin, glycerol, terpene, epoxy resins, thermal properties

2013-P09

各種木質リグニンを硬化剤に用いたエポキシ樹脂硬化物の特性

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Properties of epoxy resins hardened by woody lignins

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Abstract: We are currently researching the application of lignin extracted from steam-exploded woody biomass to epoxy resins, which is widely used as an insulating material in modern electric and electronic equipment. We have already reported the correlation between lignin properties and properties of epoxy resin hardened by lignin obtained from softwood. Here, we report the lignin properties from hardwoods and properties of hardened epoxy resin by hardwood lignin. The molecular weight of lignin extracted from hardwood decreased with higher steam pressure and longer processing time as does that of lignin extracted from softwood. The glass transition temperature of lignin-hardened epoxy resin depended on the crosslink density of the hardened resin as does that of conventional epoxy resin; however, the crosslink density differed depending on wood species. Of the four woods tested, the crosslink density of lignin extracted from *Eucalyptus globulus* was the highest, those of *Quercus acutissima* and *Phyllostachys heterocycla* were next, and that of *Cryptomeria japonica* was the lowest.

Keywords: explosion, hardwood, molecular weight, epoxy resin, crosslink density

2013-P10

リグナン生合成に関与するフェニルクマランベンジルエーテルレダクターゼ遺伝子の解析

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Analysis of a gene for phenylcoumaran benzylic ether reductase involved in lignan biosynthesis

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Abstract: Phenylcoumaran benzylic ether reductase (PCBER) is one of key enzymes for biosynthesis of 8-5’-linked lignan in seed, pollen, and vascular tissue. This enzyme catalyzes the NADPH-dependent reduction of dehydrodiconiferyl alcohol to give isodihydrodehydrodiconiferyl alcohol. It has been characterized in some plant species, such as *Forsythia intermedia*, *Pinus taeda* and *Populus trichocarpa*. Based on its sequence similarity, an *Arabidopsis* gene (At4g39230) is predicted to be a member of PCBER family. However, no biochemical evidences for the function of the encoded polypeptide was presented so far. In order to reveal the role of the gene in plant growth and development, we characterized catalytic function of the recombinant polypeptide and phenotypes of mutants in which the gene was inactivated through a T-DNA insertion. Our present results suggest that it encodes PCBER of *A. thaliana*.

Keywords: lignin, neolignan, phenylpropanoid, secondary metabolite, wood formation

2013-P11

バクテリア由来ヒドロキシ桂皮酸類 4-*O*-メチルトランスフェラーゼ遺伝子の探索

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Genome mining for hydroxycinnamic acid derivatives 4-*O*-methyltransferase encoding sequences

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Abstract: This work aims to control the lignin biosynthesis in plants using bacterial genes for the structural modification of intermediate metabolites in the monolignol biosynthetic pathway. In this study, we focused on *O*-methyltransferases (OMT), which catalyze O methylation of the *para*-hydroxyl group (4-OH) of hydroxycinnamic acid derivatives. Putative OMT genes derived from seven different bacteria were selected from the NCBI microbial genome database. These genes and *Synechocystis* OMT gene (slr0095) were synthesized with codon optimization for expression in *Escherichia coli*. Six gene products, including slr0095, were produced as soluble enzyme in *E. coli*, and purified by metal affinity chromatography. Finally we observed that three OMTs in addition to slr0095 catalyzed the 4-*O*-methylation of caffeic acid.

Keywords: biomass, metabolic engineering, caffeoyl-CoA, feruloyl-CoA, ferulic acid

2013-P12

細菌におけるリグニン由来芳香族化合物の取り込み遺伝子

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１）長岡技術科学大学・生物、２）Malaysia-Japan Int'l. Inst. Tech.

Bacterial transporters for lignin-derived aromatic compounds

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Abstract: *Sphingobiu* sp. strain SYK-6 is capable of growing on various lignin-derived aromatic compounds. The SYK-6 catabolic genes involved in the degradation of lignin-derived biaryls including 5,5′-dehydrodivanillate (DDVA), and lignin-derived monoaryls have been characterized, however, the uptake systems for lignin-derived aromatics remain unknown. In this study, we focused on the transporters for DDVA, vanillate, syringate, and ferulate. DNA microarray analysis revealed that the transcriptions of six genes, which probably encode major facilitator superfamily (MFS) transporters, were induced during the incubation with these substrates. These six genes and two other genes homologous to *pcaK* of *Pseudomonas putida* PRS2000, were disrupted in SYK-6 to determine their roles in the uptake of lignin-derived aromatics. As a result, *dvxK* mutant lost the ability to grow on DDVA but retained the ability to grow on other substrates. The deduced amino acid sequence of *dvxK* showed 21.6-25.7% identities with VanK of *Acinetobacter* sp. ADP1, PcaK of *P. putida* PRS2000, and BenK of *Corynebacterium glutamicum* RES167. These results strongly suggested that *dvxK* encodes an MFS transporter for DDVA in SYK-6.

Keywords: aromatic acid/H^+ symporter, ATP-binding cassette transporter, tripartite tricarboxylate transporter, genome mining, biomass

2013-P13

バクテリア由来コニフェリルアルデヒド二重結合還元酵素遺伝子の探索

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Genome mining for coniferyl aldehyde double bond reductase encoding sequences

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Abstract: This work aims to control the lignin biosynthesis in plants using bacterial genes for the structural modification of intermediate metabolites in the monolignol biosynthetic pathway. In this study, we focused on alkenal double bond reductases (DBR), which catalyze the reduction of the Cα-Cβ-double bond of coniferyl aldehyde. Putative DBR genes derived from six different bacteria were selected from the NCBI microbial genome database. These genes and the *Arabidopsis thaliana* DBR gene (At5g16970) were synthesized with codon optimization for expression in *Escherichia coli*. Four gene products, including At5g16970, were produced as soluble enzymes in *E. coli*, and purified by metal affinity chromatography. Finally we found that DBR of *Parvibaculum lavamentivorans* had a similar level of activity to that found in the product of At5g16970.

Keywords: biomass, metabolic engineering, α-proteobacteria, cinnamaldehyde, coniferyl alcohol

2013-P14

ジアリールプロパン型リグニン由来化合物代謝系遺伝子の単離と機能解析

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Isolation and characterization of catabolic genes for a diarylpropane-type lignin-derived compound

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Abstract: Bacterial catabolic pathway of a diarylpropane-type compound, 1,2-bis(4-hydroxy-3-methoxyphenyl)-propane-1,3-diol (HMPPD), has been reported only in *Sphingomonas paucimobilis* TMY1009, and an HMPPD-converting enzyme was purified from this strain. However, its reaction mechanism and the enzyme gene remain unknown. In this study, we investigated the HMPPD catabolism by a lignin-derived compound degrader, *Sphingobium* sp. strain SYK-6. HMPPD was degraded by both cells extracts prepared from SYK-6 cells grown in the presence and the absence of HMPPD, and vanillin and vanillate were observed as intermediate metabolites. These results suggested that the HMPPD-converting enzyme gene is constitutively expressed. Furthermore, the addition of cofactor was not required for this conversion. To isolate the HMPPD-converting enzyme gene, a gene library of SYK-6 was screened. Subcloning experiments suggested that the gene product of *aprA*, which belongs to the GMC oxidoreductase family, is an HMPPD-converting enzyme.

Keywords: biomass, biodegradation, stilbene, Cγ-elimination, Cα-dehydroxylation

2013-P15

Sphingobium sp. SYK-6 株の dehydrodiconiferyl alcohol 代謝系に関わる側鎖酸化酵素遺伝子の単離と解析

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Isolation and characterization of the genes involved in the side-chain oxidation of dehydrodiconiferyl alcohol in *Sphingobium* sp. strain SYK-6

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Abstract: The objective of this study is to identify and characterize all the *Sphingobium* sp. SYK-6 genes involved in the catabolism of a phenylcoumaran-type compound, dehydrodiconiferyl alcohol (DCA). It was proposed that SYK-6 cells degrade DCA to vanillin and 5-formylferulate through six-step reactions. We reported the isolation of the genes for the first two steps, and it was suggested that multiple alcohol dehydrogenase and aldehyde dehydrogenase genes contributed to the oxidation of DCA to DCA-C. In this study, we isolated and characterized the genes involved in the conversion of DCA-C. Based on the fact that the enzyme activity to convert DCA-C into DCA-CL was inducible, and this activity required FAD, the SYK-6 oxidoreductase genes specifically induced in the cells grown in the presence of DCA were investigated by DNA microarray analysis. As a result, *phcC* and *phcD*, which belong to the GMC oxidoreductase family, were found. Disruption of *phcC* and *phcD* in SYK-6 resulted in a decreased conversion rate of DCA-C, therefore, these genes appeared to play important roles in the degradation of DCA-C. *phcC* and *phcD* were expressed in *Escherichia coli*, and conversions of DCA-C into DCA-CL by these gene products were confirmed.

Keywords: biomass, dilignols, 8-5 dimer, bacteria, biodegradation

2013-P16

Biodegradation of petroleum crude oil by *Microphorus sp.* SM04

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Abstract: Preliminary screening using Remazol briliant blue R (RBBR) was conducted to obtain potential ligninolytic fungi in crude oil degrading. Among 82 fungi screened from nature, 12 fungi showed ability to decolorize RBBR from blue to orange color. For screening experiment, two different types of petroleum oil were used, namely heavy oil A (HOA) and heavy oil C (HOC), with two concentration (1000 and 15000 ppm). 5 Fungi (S03, S04, SM04, SM27, SM46) could grow well, both in HOC and HOA containing agar medium. Then the ablity of five fungi to degrade HOC was examined in liquid medium. In this experiment, HOC with concentration 1000 ppm was used as pollutant compounds. HOC contain aliphatic (37.5%), aromatic (36.6%), NSO (15.2%), and asphalthene fraction (10.7%). Among all fungi, isolate SM04 showed highest degradation of HOC. The degradation of aliphatic, aromatic, NSO, asphalthene fraction, and TPH by SM04 are 36.8, 22.7, 26.5, 18.2, 28.16% (15 days) and 76.4, 55.9, 46,2, 28.9, 59.3% (30 days), respectively. While TPH degradation of S03, S04, SM27, SM46 in 30 days are 37, 42, 32, 28%, respectively. Ligninolytic enzymes such as Laccase and mangan peroksidase were detected during incubation by SM04. Based on molecular identification, S03, S04, SM04, SM27, SM46 were identified as *Trametes versicolor* S03, *Ganoderma gibbosum* S04, *Microporus subaffinis* SM04, *Bjerkandera adusta* SM27, and *Bjerkandera adusta* SM46.

Keywords: Petroleum crude oil, biodegradation, ligninolytic enzymes, white rot fungi, *Microporus sp.*

2013-P17

ジャトロファ種子の搾油カス由来のカテコール型リグナン･ネオリグナンについて

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Catechol-type lignan/neolignans isolated from the defatted seed residue of Jatropha

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Abstract: Jatropha (*Jatropha curcus*) is a shrub for biodiesel fuel production. From the defatted seed residue of Jatropha, eight antioxidative lignan/neolignans which have catechol rings were isolated. Their structures, stereochemistry, and biosynthesis are discussed as compared with those of products by enzymatic and non-enzymatic dehydrogenation of caffeyl alcohol.

Keywords: *Jatropha curcus,* biodiesel fuel; antioxidant, caffeyl alcohol, 3,3’-bisdemethylpinoresinol

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2014-101

リグニン生合成中間体としてのモノリグノールグルコシド

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Monolignol glucosides as intermediate compounds in lignin biosynthesis

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Abstract: A large amount of monolignol glucosides (*p*-glucocoumaryl alcohol, coniferin, syringin) are found in lignifying soft xylem near cambium, and they disappear with the progress of lignification. Recently, it became a matter of debate whether those monolignol glucosides are the real intermediates to form macromolecular lignin or only a storage form of monolignol out of the main biosyntheic pathway. The exclusion of monolignol glucosides from the main pathway is derived from the wrong explanation of incorrect experimental procedures and too simple explanation of experimental result for flexible biological phenomena "lignification". In this paper, we reconfirmed the most basic pathway of lignin biosynthesis starting from L-phenylalanine to lignin via monolignol glucosides, and proposed a hypothetical scenario for 3D assembly process of cellulose, hemicellulose and lignin in the lignifying cell wall. Advantages of monolignol glucosides as the intermediates in formation of macromolecular lignin are summarized as follows: (1) They are water soluble and so stable in oxidative environment that they are suitable for delivery to lignifying site through the preformed thick polysaccharide gel. (2) β-D-Glucosidase specific to a specific glucoside can control formation of designed lignin supra- molecule according to the time, place and occasion (TPO). (3) Storage in large amount, often in crystalline form as an big metabolic pool, is advantageous for formation of a massive architecture in TPO, e.g. postmortem lignification, late wood formation etc. (4) Slow turnover of monolignol glucoside, namely slow fixation of ultrastructure in secondary wall (responsible for stem strength) supplied from the large metabolic pool is advantageous for maintaining the stem in proper positions (reaction wood). (5) It is advantageous also for plant that slow lignification in the secondary wall causes gradual ejection of water by which Ca^{++} and enzymes are transfered toward lumen side, and finally they are recovered for nitrogen economy.

Keywords: metabolic pool, cell wall architecture, *Ginkgo*, *Magnolia*,

2014-102

生体直交型反応を活用したリグニンのメタボリックラベルと蛍光標識

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A bioorthogonal chemistry strategy for visualization of cell wall lignification

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Abstrct:Bioorthogonal click chemistry was commissioned to visualize the plant cell wall lignification process *in vivo*. This approach uses synthetic monolignol mimics tagged with chemical reporters (azide and alkyne groups) that can be metabolically incorporated into lignins in live plants, and subsequently derivatized via *in vivo* click reactions, i.e., copper-assisted azide-alkyne cycloadditions or "copper-free" strain-promoted azide-alkyne cycloadditions.

Keywords: *Arabidopsis thaliana*; cell wall; fluorescence microscopy; *in vivo* imaging; lignin biosynthesis.

2014-103

ミズナラ落葉の冬季生分解過程におけるリグニンの挙動

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Qualitative and quantitative monitoring of lignin in leaf litter of Japanese oak tree (*Quercus mongolica* var. *grosseserrata*) during the biodegradation process in winter

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Abstract: An improved method to monitor lignin in leaf litter has been proposed, with a combination of two methods to determine methoxy group and alkaline nitrobenzene oxidation products. Our results provided additional evidence that conventional methods for lignin determination, such as Klason and acetyl bromide methods, gave an overestimated value of lignin content, as repeatedly indicated in earlier studies. Next, the authors tried to monitor the changes in lignin in leaf litter qualitatively and quantitatively during its biodegradation process including wintertime, using our combined method. It was confirmed that while leaf litter was decomposed progressively under snow cover during wintertime, lignin in leaf litter was also degraded accordingly, indicating leaf lignin-degrading microbes were active in soil organic matter at around 0 °C. Contrary to the previous observation, lignin content of leaf litter was steadily and gradually decreased in the course of time, to a comparable degree as the other leaf components. This result suggests foliage lignin is not as recalcitrant as has been supposed. Interestingly, condensed lignin structures, supposedly less biodegradable than non-condensed structures of lignin, were also decreased to a comparable degree.

Keywords: foliage lignin, leaf litter, carbon cycle, biodegradation, Japanese oak (*Quercus mongolica* var. *grosseserrata*)

2014-104

樹木の葉から得られるクラーソン残渣のメトキシル基の分析

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Methoxyl analysis of Klason residue of tree leaves

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Abstract: In previous studies, it was strongly suggested that Klason method overestimates the lignin content of non-wood tissues or plants due to the inclusion of non-lignin substances in Klason residue and that no pre-extraction method could remove these non-lignin substances selectively. In this study the behavior of methoxyl group in leaf samples during extraction was examined.

Amount of methoxyl group in Klason residue of leaf samples were extremely lower than that of woodsamples. By various kind of pre-extraction, the amount of methoxyl group in Klason residue of leaves was found to decrease when it was expressed as non-extracted sample basis value. This result indicated that a part of substances which contains methoxyl group and participates in the formation of Klason residue can be removed by these pre-extraction. Amount of methoxyl group found in nitrobenzene oxidation products was also examined for leaf samples before and after various pre-extraction. In case of wood sample, the amount of methoxyl group found in nitrobenzene oxidation products should be lower than that found in Klason residue and should not change significantly by pre-extraction. However, the amount of methoxyl group found in nitrobenzene oxidation products decreased by pre-extraction almost proportionally to that found in Klason residue.

Keywords: leaf, Klason residue, methoxyl group, extraction

2014-105

樹種間におけるビフェニル型構造量の多様性

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Variety of the content of biphenyl structures among different wood species

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Abstract: Although biphenyl structure is important structural unit as a candidate of branch-points of lignin, limited information is available for the content of biphenyl structures. In this study, 21 kinds of wood meals including 6 softwood and 15 hardwood species were analyzed by alkaline nitrobenzene oxidation method to investigate the variety of the content of biphenyl structures among different wood species. In the case of the softwoods, the total yields of biphenyl products varied within a narrow range (0.030-0.035 mol/200 g lignin), in which the yield was slightly lower in a species having a lower methoxyl content of lignin. In contrast, the total yields of biphenyl products ranged widely among hardwood species (0.0012-0.023 mol/200 g lignin). The hardwood species having a higher syringyl/guaiacyl ratio exhibited a lower biphenyl products yield, and a lower yield ratio of biphenyl products to all the guaiacyl type degradation products. The latter tendency implies that, during lignin polymerization, the frequency of 5-5 coupling reaction between guaiacyl units was not constant, but lowered by cross-coupling reaction between syringyl and guaiacyl units when syringyl content is higher.
Keywords: lignin biosynthesis, divanillin, 5-5 linkage, gymnosperm, angiosperm

2014-106

クラフトパルプの過硫酸処理における残留リグニンの分解挙動

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Behavior of residual lignin during peroxymonosulfuric acid treatment of kraft pulp

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Abstract: Conversion of chlorine process into Elemental chlorine-free (ECF) bleaching is known to be efficient for reducing the amount of organic chlorine compound in effluent to significant extent. However, biodegradability of the organic chlorine compound in mill effluent should be more improved because mills still release organochlorine substances. ECF bleaching is still discharging organochlorine substances, especially chloroform by volatilization. On the other hand, total chlorine-free (TCF) bleaching is a process that eliminates possibility of organochlorine compound formation in bleaching process. Peroxymonosulfuric acid (MPS) has been identified as one of promising alternative chemicals for delignification of wood and bleaching. It is capable to oxidize and solubilize lignin and also to decompose hexenuronic acid (HexA), which is one of the compounds resulting in pulp yellowing. MPS also can be produced on industry scale with high stability and successfully installed in mills as a conversion of acid washing stage of ECF bleaching. MPS treatment was conducted with 10% pulp consistency at pH 3 and 70ºC for 70 min. The application of MPS indicated that pulp brightness increased to 84-86%ISO with 0.1-0.5% MPS dosage by the Oxygen-MPS-Ozone-Extraction-Peroxide bleaching. In this study, we investigated effects of the application of MPS on decrease of HexA and kappa number, and on decomposition behaviors of vanilliyl alcohol and syringyl alcohol and other lignin model compounds.
Keywords: pulp bleaching, peracid, viscosity, *Acacia*, dissolving pulp

2014-107

オイルパーム幹のアルカリ/グリセリン蒸解によるパルプとリグニンの特性

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Characterization of pulp and lignin prepared from oil palm trunk by the alkaline/glycerol pulping

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Abstract: The oil palm tree has widely planted for the production of edible oil in South East Asian countries such as Indonesia and Malaysia. In those countries, large amount of oil palm waste is constantly produced due to its plantation cycle. For the effective utilization of these waste biomass as a raw material of biomass energy and material productions, oil palm trunk was cooked in alkaline/glycerol, which could be produced as by-products of biodiesel production, to separate it into the components, carbohydrate and lignin. In the alkaline/glycerol process, lignin was effectively removed in comparison with alkaline cooking process. Pulp yield in the alkaline/glycerol process was also higher than that in the alkaline cooking process. The alkaline/glycerol process would be a good method for component separation of the oil palm trunk.

Keywords: oil palm trunk, alkaline/glycerol, pulp, hemicellulose, lignin

2014-108

リグノセルロース酵素糖化に及ぼす試料加熱前処理の効果

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Drying temperature on rice straw affects the enzymatic saccharification efficiency

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Abstract: In order to use lignocellulose for polysaccharide, the pretreatment of plant materials is required. Usually, the pretreatment of plant materials after harvesting is drying, grinding and powdering. The effects of grinding on saccharification efficiency have been studied intensively. However, the first step of pretreatment, namely drying has not been noted. In this study, we estimated the effect of drying temperature on enzymatic saccarifiation efficiency. After harvesting of rice (*Oryza sativa*), rice straws were dried at 27˚C, 50˚C and 70˚C during 31, 5 and 4 days, respectively. The enzymatic saccharification efficiency was 45.1, 45.6 and 41.6%, respectively under each temperature. Obviously, the efficiency of pretreatment under 70˚C drying was decreased. It is well known that many polymers change their shape with temperature rising. The glass transition point of lignin is 60 - 70˚C under a high water content condition. Our results strongly suggested that the high drying temperature caused plasticization of lignin and extra encrustation of cellulose microfibrils by lignins, which resulted in decreasing of accessibility of hydrolyzing enzymes to cellulose.

Keywords: rice straw, drying temperature, lignin, lignocellulose, saccharification

2014-109

ソフト水熱プロセスによるきのこ廃培地中の水／アセトニトリル可溶性低分子の挙動

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Behaviors of the water/acetonitrile-soluble low-molecular-weight compounds in the soft-hydrothermal processing of the waste culture media of edible mushrooms

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Abstract: Lignin is a potential sustainable resource of non-petroleum natural aromatic chemicals. The waste culture media of the edible mushroom are the plausible candidates as raw materials containing partially degraded lignin. Recently, we succeeded the microbial production of the aromatic monomer of phenyl-propane structure from the waste culture media of the edible mushroom, *Hypsizygus marmoreus*, Bunashimeji. The yield was elevated after the pretreatment by the soft-hydrothermal processing of the starting raw materials. In this study, we traced the water/acetonitrile-soluble low-molecular weight compounds during the pretreatment using the LCMS analysis. Multivariate statistical analysis revealed the behavior of aromatic monomers which were consumed along with the growth of *H. marmoreus* and regenerated by the soft-hydrothermal processing. The LCMS analysis coupled with the chemometrics procedures was a robust tool to summarize and visualize the complex components of the bioresources.

Keywords; bacteria, beta-O-4, biorefinery, enzyme, principal component analysis

2014-110

スギ炭化物及びそのアセチル化処理試料に吸着したセシウムイオンの可視化

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Visualization of the cesium ions adsorbed onto Japanese cedar charcoals and their acetylated samples

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Abstract: To visualize the distribution of cesuim ions (Cs$^+$) adsorb onto Japanese cedar charcoals carbonized at 300°C, 500°C, and 700°C under N$_2$ flow, respectively, Scanning electron microscopy and Energy dispersive X-ray (SEM-EDX) analysis was applied to these samples. After soaking in saturated aqueous CsCl solution, these samples were embedded in Technovit 7100 to make a thin section (1 □m) for the observations of Cs$^+$ by SEM-EDX analysis. As a result of the Cs$^+$ observations, Cs$^+$ adsorb onto the all samples could be seen with a sufficient contrast. Each charcoal sample treated by acetylation was also prepared in the same procedure. However, Cs$^+$ on these samples could not be seen with a sufficient contrast. It was suggested the possibilities that the protection of alcoholic hydroxyl groups and phenolic hydroxyl groups on these charcoal surfaces could affect the Cs$^+$ adsorption involved in the ion-exchange sites of these groups, and that the Cs$^+$ adsorption involved in the Wan der Waals force and ion-exchange sites of carboxylic groups might be affected by the steric hindrance of acetyl groups introduced on the charcoal surface. Since introduction of acetyl groups on the charcoal surface apparently affected the Cs$^+$ adsorption, ester structure of introduced acetyl groups were assumed to be less interaction with the Cs$^+$.

Key word: line analysis, torrefaction, microtome, functional group, compound middle lamella

2014-111

リグニンの精製によるリグニン硬化エポキシ樹脂の高 Tg 化

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Improvement of the glass transition temperature of epoxy resin hardened by steam-exploded lignin

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Abstract: We are currently researching the application of lignin extracted from steam-exploded woody biomass to epoxy resins, which is widely used as an insulating material in modern electric and electronic equipment. We have already reported that the glass transition temperatures of hardened epoxy resin containing lignin were higher than those of commercially available epoxy resins, and that the electric and heat resistance properties of epoxy resins hardened with steam-exploded lignins are equivalent to those of conventional epoxy resin.. Here, we report improvement of the glass transition temperature of epoxy resin hardened by steam-exploded lignin. The decomposition temperature of steam-exploded lignin could be improved by reducing low-molecular-weight compounds contained in the steam-exploded lignin. The glass transition temperature of epoxy resin hardened by steam-exploded lignin was also improved by refinement of steam-exploded lignin or wood feedstock prior to the steam explosion. On the other hand, the decomposition temperature of epoxy resins hardened by steam-exploded lignins was not improved by the refinement. It was suggested that the thermal decomposition of hardened epoxy resin is primary caused by the decomposition of lignin.

Keywords: steam explosion, glass transition temperature, epoxy resin, heat resistance

2014-112

スギ加溶媒分解リグニンを用いた新規ポリエステルフィルムの調製とその応用

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Preparation and application of a new polyester film from cedar-organosolv lignin

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Abstract: A new polyester film based on the melt-polymerization of softwood organosolv lignin was fabricated by hot pressing, with varying molar charge ratio of maleic anhydride to hydroxy group of the lignin. This organosolv lignin was directly isolated by a solvolysis of cedar chips with polyethylene glycol 400 (PEG400) and a small amount of sulfuric acid as a catalyst, and showed a thermal fusibility. At a certain charge ratio of 6.6/3.4, tensile strength and young modulus were shown to be the maximum values of 45.6 MPa, and 2.4 GPa, respectively. Moreover, we assembled an electric double layer capacitor (EDLC) containing this film as a separator, to investigate the application of this polyester film. Although the resulting EDLC didn’t show a good performance when the polyester film was used without further modification, formation of pores on the film improved the electrochemical property of EDLC; the specific capacitance reached nearly 80 % of the one with a commercial cellulose separator. These results indicate this lignin-based polyester film can be utilized as a separator material for the EDLC.

Keywords: organosolv lignin, melt polymerization, EDLC separator

2014-113

リグニン系活性炭素繊維を原料とする電気二重層キャパシタ用電極の開発

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Development of electrode for electric double layer capacitor from lignin-based activated carbon fibers

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Abstract: In the lignin symposium last year, we reported to prepare activated carbon fibers (ACF) from hardwood acetic acid lignin and to assemble electric double layer capacitor (EDLC) with the ACF and organic electrolyte together with conductive carbon black. In this study, such EDLCs were prepared from two kinds of isolated softwood (Japanese cedar) lignins, soda (SL)-lignin and PEG-lignin, via electrospinning. Although we expected that thin fibers prepared by electrospinning would be easily converted to ACF with very large surface area, electrospun SL-lignin fibers were converted to ACF with lower BET surface area than the ACFs from other types of lignin fibers which were thicker. Due to this fact, EDLC assembled with the SL-lignin-based ACF had inferior electrochemical performance to the EDLCs with ACFs from other lignin-based ACF. On the other hand, EDLC with PEG-lignin-based ACF showed moderate electrostatic capacitance, and noticeably low charge transfer resistance. In this symposium, we will further discuss the relationship between electrostatic capacitance of EDLC and pore structure of ACF.

Keywords: cedar, electrode for electric double layer capacitor, electrospinning, PEG-lignin, soda-lignin,

2014-特別講演

触媒の発見から実用化まで、～クリーン酸化、テルペンやセルロースの変換、砂の資源化～

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Green oxidation with hydrogen peroxide

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Abstract: Oxidation is a core technology for converting petroleum-based materials to useful chemicals of a higher oxidation state. Aqueous hydrogen peroxide (H_2O_2) is an ideal oxidant, because the atom efficiency is excellent and water is theoretically the sole co-product. However, H_2O_2 can be a clean oxidant only if it is used in a controlled manner without organic solvents and other toxic compounds. Thus, the discovery of an efficient catalyst and the choice of reaction conditions are the keys to realizing an ideal oxidation procedure. In this context, we developed various oxidation reactions with aqueous H_2O_2 under organic solvent- and halide-free conditions.

Keywords: catalyst, cellulose, organosilicon, insulating resin, levulinic acid

2014-201

β-*O*-4 型リグニンモデルオリゴマーの合成研究

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Synthetic study on β-*O*-4 type lignin model oligomer

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Abstract: Artificial lignin polymers with β-*O*-4 linkages have been synthesized in our laboratory. In this study two synthetic strategies: convergent and linear syntheses were evaluated for the synthesis of β-*O*-4 type lignin model oligomer with distinct degree of polymerization. A key reaction step was Williamson ether formation, which includes nucleophilic substitution under basic conditions. Effect of several bases and protective groups were investigated and a tetramer was synthesized by the linear synthetic strategy.

Keywords: Synthesis, □-O-4, tetramer, trimer, dimer

2014-202

酸性条件下におけるベンジルカチオンの生成挙動

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Formation behavior of benzyl cation of lignin model compounds under acidic conditions

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Abstract: In this study, it was examined how the difference between *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) or between phenolic (P) and non-phenolic (N) nuclei controls the formation rate of benzyl cation under acidic conditions using model compounds, 2-(4-hydroxy- benzyloxy)ethanol (HP), 2-(4-methoxybenzyloxy)ethanol (HN), 2-(4-hydroxy-3methoxybenzyloxy) ethanol (GP), 2-(3,4-dimethoxybenzyloxy)ethanol (GN), 2-(4-hydroxy-3,5-dimethoxybenzyloxy) ethanol (SP), and 2-(3,4,5-trimethoxybenzyloxy)ethanol (SN). The disappearances of all the model compounds were well approximated to pseudo-first-order reactions. The pseudo-first- order reaction rate constants of the model compounds with H, G, and S nuclei were in the order of: H > G > S. On the other hand, the P type model compounds disappeared much faster than the N type model compounds. These results suggest that benzyl cation is generated most rapidly from H nucleus and most slowly from S nucleus and that P type nucleus affords benzyl cation much more rapidly than N type nucleus.

Keywords: wood, acidolysis, carbo cation, carbenium ion

2014-203

非フェノール性 β-エーテル型リグニン二量体モデル化合物の熱分解反応機構 ー側鎖水酸基に起因するレトロアルドール反応ー

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Pyrolysis mechanism of a non-phenolic β-ether type lignin model dimer ーRetro-aldol reactions occurring at the side-chainー

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Abstract: Influence of the Cγ-OH group on the pyrolytic reactivity of non-phenolic β-ether type lignin model dimer was studied in ampoules under the condition of N_2/350℃/2min. Although the Cγ-deoxy type dimer became reactive only in the presence of wood flour as a radical source, the Cγ-OH type dimer degraded even without the addition of any radical sources. Furthermore, the pyrolysis products were very different depending on the Cγ-structure; the major products from the Cγ-deoxy type had C3 side-chains, while the products from the Cγ-OH type contained shorter C1 and C2 side-chains. Based on these results, two types of retro-aldol reactions were suggested for the pyrolysis of the Cγ-OH type dimer. These reactions are discussed with the side-chain conversions and depolymerization of natural lignins during pyrolysis. The results of the theoretical investigations indicated an interesting feature of these retro-aldol reactions; the reactivity is very different depending on the stereochemistry of the side-chain, i.e., *erythro* and *threo* types.

Keyword: pyrolysis, retro-aldol reaction, depolymerization, stereochemistry, theoretical investigation

2014-204

２次元 NMR による天然試料のフェニルグリコシド型 LCC の化学構造解析

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2D NMR analysis of lignin-carbohydrate complex (LCC) in *Eucalyptus globulus*

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Abstract: The *Eucalyptus globulus* wood meal was separated into 12 fractions via multi-step solvent extractions, and the distributions and structures of lignins and carbohydrates in the each fractions were profiled using 2D NMR techniques. Our NMR data suggest that lignins mainly composed of syringyl β–*O*–4 units are tightly associated with xylans in *Eucalyptus* wood cell walls. A newly constructed, NMR database based on synthetic model for phenyl glycoside type lignin-carbohydrate linkages were applied to delineate lignin-carbohydrate complex (LCC) possibly present in *Eucalyptus* wood cell walls.

Keywords: lignin-carbohydrate complex (LCC), xylan, phenyl glycoside, *Eucalyptus globulus*, HSQC NMR

2014-205

ジヒドロコニフェリルアルコールの脱水素重合とその結合様式

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Dehydrogenative polymerization of dihydroconiferyl alcohol and its chemical sturucture

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Abstract: Cβ-radical mesomeric hybrid of the phenoxy radical of coniferyl alcohol is the most important intermediate during the dehydrogenatiive polymerization of lignin, because Cβ-radical is involved in the formation of β-*O*-4, β-5 and β-β substructures of lignin macromolecules. When coniferyl alcohol is reductively converted to dihydroconiferyl alcohol without the side chain double bond, the generation of Cβ radical becomes impossible, and it is expected that lignin biosynthesis greatly changes. In this study, we performed an *in vitro* polymerization of dihydroconiferyl alcohol (DC-DHP). DC-DHP exhibited lower degree of polymerization than coniferyl alcohol DHP and considerable amount of dihydroconiferyl alcohol oligmers was formed. Frthermore, it was revealed that the major compound of the oligmeric fraction was a dimer having 4-*O*-5 linkage.

Keywords: dihydroconiferyl alcohol, lignin biosynthesis, double bond reductase, lignin substructure

2014-206

細菌のピノレジノール還元酵素遺伝子を用いた植物の芳香族化合物代謝の改変

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Metabolic engineering of plant phenolic compounds by heterologous expression of a gene for pinoresinol reductase in transgenic plants

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Abstract: Pinoresinol reductase and pinoresinol/lariciresinol reductase play important roles in an early step of lignan biosynthesis in plants. The activities of both enzymes have also been detected in bacteria. In this study, *pinZ*, which was first isolated as a gene for bacterial pinoresinol reductase, was constitutively expressed in *Arabidopsis thaliana* with and without apoplast-targeting sequence (ATS) under the control of the cauliflower mosaic virus 35S promoter. Higher reductive activity toward pinoresinol was detected in the resultant transgenic plants but not in wild-type plants. The activity was higher in the transgenic plants harboring the transgene attached without ATS than that with ATS. Principal component analysis of data from untargeted metabolome analyses of tissue extracts of the wild-type and two independent transgenic lines with *pinZ* without ATS indicate that *pinZ* expression caused dynamic metabolic changes in stems, but not in roots and leaves. Amounts of pinoresinol and its glucoside form in soluble extracts of the tissues were markedly reduced in the transgenic plant with highest PinZ activity, whereas the amounts of glucoside form of secoisolariciresinol increased. Our findings indicate that overexpression of *pinZ* induces change in lignan compositions and has a major effect not only on lignan biosynthesis but also on biosynthesis of other primary and secondary metabolites. Structural analysis of lignin in the transgenic plans is now in progress.

Keyword: gene expression, secondary metabolite, transgenic plant

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2014-207

Sphingobium 属細菌の dehydrodiconiferyl alcohol 代謝系遺伝子の単離と機能解析

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Isolation and characterization of dehydrodiconiferyl alcohol catabolism genes in *Sphingobium* sp. strain SYK-6

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Absract: The objective of this study was to identify and characterize the *Sphingobium* sp. SYK-6 genes involved in the catabolism of a phenylcoumaran-type compound, dehydrodiconiferyl alcohol (DCA). In SYK-6 cells, the alcohol group at the γ-carbon of the B-ring side chain of DCA was oxidized to the carboxyl group to generate DCA-C. The resulting DCA-C was converted to DCA-CC by the oxidations of the alcohol group at the γ-carbon of the A-ring side chain of DCA-C. DCA-CC was degraded to 5-formylferulate and vanillin through the release of γ-carbon and the cleavage of the Cα-Cβ linkage of the A-ring side chain. In the first two steps, the multiple genes encoding alcohol dehydrogenases and aldehyde dehydrogenases were identified as possibly being involved in the conversion processes. The *phcC* and *phcD* genes, which belong to the GMC oxidoreductases, were identified as candidate genes responsible for the oxidation of DCA-C. Disruption of *phcC* and *phcD* in SYK-6 resulted in a decrease in the rate of DCA-C conversion, indicating that these genes play important roles in the degradation of DCA-C. Conversion of DCA-C by the gene products of *phcC* and *phcD* was confirmed using recombinant proteins produced in *Escherichia coli* and SYK-6.

Keywords: dilignol, β-5, biodegradation, catabolic pathway

2014-208

高活性リグニン分解菌 *Phanerochaete sordida* YK-624 株のリグニン分解過程におけるトランスクリプトーム解析

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Transcriptome analysis in lignin degradation process by hyper lignin-degrading fungus *Phanerochaete sordida* YK-624

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Abstract: The mechanism of lignin biodegradation by white-rot fungi has been extensively studied. However, the whole process is still unknown. In particular, it is interesting that why the white-rot fungus *Phanerochaete sordida* YK-624 indicates high lignin-degrading activity. In order to identify genes which are involved in lignin biodegradation by *P. sordida* YK-624, we analyzed the differential gene expression of *P. sordida* YK-624 under the ligninolytic and non-ligninolytic conditions by next generation sequencing. Total RNA was extracted from the wood (ligninolytic) and holocellulose (non-ligninolytic) medium. After the construction of cDNA library, short read sequence data (300 bp read length) were obtained using MiSeq. We obtained high-quality read sequences by removing regions with low quality scores in fastq files (quality scores < 30). The high-quality short reads from samples were assembled into unigenes (contigs, a non-redundant sequence set) by program Trinity. To detect genes showing different gene expression levels, we investigated expression levels by FPKM (Fragments Per Kilobase of exon per Million mapped reads) measurement. Biological functions of differential unigenes were predicted by BLAST, Gene Ontology and KEGG pathway analyses. As the results of the differential gene expression analysis, manganese peroxidase and glyoxal oxidase which were related to lignin biodegradation were upregulated under the ligninolytic condition. On the other hand, some genes such as oligopeptide transporters which have not been previously reported in lignin biodegradation were also upregulated under the ligninolytic condition.

Keywords: *Phanerochaete sordida* YK-624; lignin biodegradation; differential gene expression; Miseq

2014-209

Biodegradation of polycyclic aromatic hydrocarbons mixture by *Pestalotiopsis* sp.

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Abstract: The ability of *Pestalotiopsis* sp. NG007 to degrade and transform PAHs was examined using four PAHs: acenaphthene (ACE), anthracene (ANT), chrysene (CHRY), and benzo[a]pyrene (BaP) in liquid medium. The experiments were conducted in different pH (3 – 12) and salinities (0 – 10%). The results showed that the biodegradation of PAHs mixture was dependent to pH and salinities. All the PAHs showed a maximum degradation at pH 3 and salinities 2–2.5%. The maximum removal for ACE, ANT, CHRY, and BaP were 100%, 91%, 76%, and 68%, respectively. In general, the biodegradation capacity decreased with the increasing of ring number in PAHs. Analysis of metabolites using GC-MS showed at least 11 compounds were detected. Strain NG007 degraded ACE via the formation of 1-acenaphthenol (I), acenaphthenon (II) and naphthalic anhydride (III). The presence of anthraquinone (IV) in the culture can be identified as a metabolite from ANT degradation. In addition, the presence of 1-hydroxy-2-naphthoic acid (V) may indicate the metabolism of CHRY and BaP. Other compounds such as gentisic acid (VI), mandelic acid (VII), phthalic acid (VIII), cathecol (IX), benzaldehyde (X), and benzoic acid (XI) indicated that the biodegradation of the major metabolites into small compounds was occurred. This study demonstrated that strain NG007 can degrade all the PAHs in the mixture and may consider to have the potential for degradation of PAHs in contaminated environments.

Keywords: biodegradation, ligninolytic enzymes, PAHs, *Pestalotiopsis* sp., saline

2014-P01

芳香核 1 位 ^{13}C 標識コニフェリルアルコールの新規合成方法の検討

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Investigation of new synthesis approach of coniferyl alcohol-[ring-1-^{13}C]

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Abstract: It is difficult to isolate lignin without modification because of its complexity, nonuniformity, and conjunctive bonding to other substances. In order to analyze lignin structure, a technique of specific ^{13}C-enrichment of cell wall lignin prepared by administration of ^{13}C-labeled monolignol glucosides combined with NMR has been employed. In recent studies, labeling of side chain-α, -β, and-γ, and of ring-3, -4, and -5 of the lignin precursors have been succeeded. ^{13}C labeled monolignol at ring-1 was also prepared in the previous research. However, the yield was very low, so a new method of synthesis of monolignol-[ring-1-^{13}C] is required for lignin structure analysis. In this study, we investigated the new synthesis approach of coniferyl alcohol-[ring-1-^{13}C].

Keywords: coniferyl alcohol, 2D-NMR, ^{13}C-labeling, synthesis route, lignin

2014-P02

α-Keto / β−*O*−4 構造を有する phenyl glycoside 型 LCC モデル化合物の合成

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Synthesis of dilignol β-glycosides with α-keto / β−*O*−4 structures

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Abstract: A series of α-keto / β-*O*-4 dilignol β-D-glycosides were synthesized as model for phenyl glycoside type lignin-carbohydrate (LC) linkages possibly present in plant cell wall. α-Keto guaiacylglycerol-β-guaiacyl ether derivative (**1G**) was acetylated to give compound **2G** (94.5%). The compound

2G was treated with 5% Pt/C catalytic reduction to afford compound **3G** (61.8%). The glycosylation of compound **3G** with compound **4** by imidate method afforded only β-D-glycoside **6G** (64.7%). Deacylation of compound **6G** with NaOMe / MeOH gave target compound **8G** (43.5%). The synthetic method for compound **8G** was applied to the syntheses of other β-D-glycosides. The fully assigned NMR spectra of guaiacyl and syringyl α-keto / β-*O*-4 dilignol β-D-glycosides and β-D-xylosides provided useful database information for peak assignment and authentication that could be readily implemented for the analysis of LC linkages in plant cell walls using high resolution NMR techniques.

Keywords: lignin-carbohydrate complex (LCC), 2D HSQC NMR, phenyl glycoside, dilignol, α-keto dilignol, β-*O*-4 dilignol

2014-P03

Laser microdissection を用いたポプラ木部の成長輪内におけるリグニン解析

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Lignin analysis in growth ring of *Populus alba* xylem using Laser microdissection

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Abstract: Lignification is a cell wall fortifying process, which occurs in xylem tisssue before programmed cell death (PCD). It was reported that some genes related in monolignol biosynthesis were expressed in ray parenchyma cells in the lignified area. It was also observed that CWPO-C that is capable of lignin polymerization located in the cell corners of the mature fiber cells. These results suggest that lignification still proceeds in the fiber cells after their programmed cell death. Acetocarmine staining of nuclei and fragments of DNA was not observed in the cells within the area between the 20th or 30th cells from cambial and the pith, suggesting the fiber cells in this area were already suffered from PCD. The pyrolysis product and S/G ratio derived from β-O-4 linked lignin in the dissected samples of Populus alba xylem using laser micro dissection were determined by Py-GC-MS. The increase of pyrolysis production and decrease of S/G ratio along with the radial direction within a growth ring suggest that lignification in the fiber cells may continue even after PCD with the assistance of ray parenchyma cells.

Keywords: acetocarmine, biosynthesis, lignification, laser microdissection, pyrolysis-GC-MS,

2014-P04

A. thaliana を用いたモノリグノール輸送に関わる輸送体の探索

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Screening of monolignol transport protein in *A. thaliana*

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Abstract: Monolignols are synthesized in the cytosol and transported to the cell wall to biosynthesize linign. It was reported that one of ATP-binding cassette (ABC) proteins, *AtABCG29*, is involved in the transportation of *p*-coumaryl alcohol, however, there have been no report on other monolignols for guaiacyl and syringyl lignin, which are major constitute units of angiosperm lignin. In this study, 9 genes including ABC proteins were selected as monoligol transport candidates among the genes those expressions were largely changed during the tracheary element differentiation of Arabidopsis cell culture, and T-DNA insert mutants of these genes were subjected to lignin analyses. There were no difference in both lignin content and S/G ratio between wild type and each knockout mutant. The expression analysis of each gene in the several organs did not show specificity in the stem unlike *ABCG29.* These results suggest that the candidate genes may not be involved in monolignol transportation in the Arabidopsis stem.

Keywords: ABC protein, *Arabidopsis thaliana*, lignification, monolignol transporter, tracheary element

2014-P05

リグニンのビフェニル型分岐構造の探索: モデル実験と NMR(HMBC)測定条件の検討

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Exploring biphenyl-type branch-points in lignin; model experiments and the examination of NMR (HMBC) measurement condition

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Abstract: For the purpose of exploring non-phenolic dibenzodioxocin (5–5/4–O–β, DBDOX) structures as a candidate of branch-points in lignin, measurement condition of a long-range ^{13}C–^{1}H correlation NMR (HMBC) experiment was examined using acetylated pine MWL ($CDCl_3$). Although Hα/C1 correlation peak of phenolic DBDOX was detected under the conditions of 71-111 ms long range coupling delays, that of non-phenolic DBDOX was not found in the present study. As a model experiment, a coupling reaction using peroxidase and hydrogen peroxide system was examined if or not phenolic DBDOX model compound couples with coniferyl alcohol (CA). While a substantial amount of G-GG–type DBDOX model remained after one day, S-GG–type DBDOX model almost disappeared in a shorter reaction time.

Keywords: 5-5 linkage, biphenyl structure, soft wood, milled wood lignin, 2D NMR

2014-P06

アルカリ蒸解過程におけるリグニン β-O-4 結合開裂の速度論的検討（3）

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Kinetic analysis of the β-O-4 bond cleavage of lignin during alkaline cooking process (3)

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Abstract: It was quantitatively investigated how the structural differences between *p*-hydroxyphenyl, guaiacyl and syringyl aromatic nuclei and between the *erythro* and *threo* isomers in the side chain part of β-O-4 bond affect the rate of the β-O-4 bond cleavage. As model compounds, dimeric C_6-C_2 type non-phenolic β-O-4 types were used, and the obtained results were compared with those of the C_6-C_3 type analogues, which were obtained in our previous studies. The effect of the presence of γ-hydroxymethyl group on the β-O-4 bond cleavage rate can be examined by comparing the C_6-C_3 and C_6-C_2 type model compounds. In most cases, the disappearance rate was in the order of: C_6-C_3 *erythro* compounds > C_6-C_2 compounds > C_6-C_3 *threo* compounds, when their aromatic nuclei are the identical. The presence of a syringyl nucleus enhanced the β-O-4 bond cleavage rate in the reaction of not only the C_6-C_3 but also C_6-C_2 type model compounds. These results may suggest that steric factor resulting from the presence of syringyl nucleus affects the cleavage rate even when γ-hydroxymethyl group is absent.

Keywords: alkaline hydrolysis, alkyl-aryl ether, cooking, configuration, kraft pulping, wood delignification

2014-P07

NMR および LC/MS/MS によるバガス中リグニンの構造解析と GPC によるバガス中セルロースの平均重合度分析

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Structural analysis of lignin in bagasse by NMR and LC/MS/MS, and analysis of the number-average degree of polymerization of the cellulose in bagasse by GPC

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Abstract: The structure of cellulose and lignin in bagasse were determined by NMR, and it was confirmed that aromatic carbon derived from lignin and aliphatic carbon derived from hemicellulose existed. The structure of compounds in extracted solution detected by LC/MS/MS were estimated as a degradation products of lignin. The number-average degree of polymerization in cellulose derived from bagasse were evaluated by modified BCA method and GPC-MALS, and those results showed correlation each other. Because the modified BCA method can obtain analysis results more quickly than GPC-MALS, it is possible to use it as the screening measurement of the number-average degree of polymerization.

Keywords: CP/MAS, dipolar dephasing, multivariate statistics

2014-P08

糖化残渣中のリグニンの特性に及ぼす糖化前処理の影響

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Effects of pretreatments of saccharification on characteristics of lignin in saccarification residue

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Abstract: Lignin residues produced from saccharification with hydrothermal-mechanochemical pretreatment were analyzed by alkaline nitrobenzene oxidation. The sum of vanillin and syringaldehyde detected by alkaline nitrobenzene oxidation treatment decreased with the hydrothermal reaction time of more than 2 hours. Lignin extracted from re-hydrothermal treated saccharification residue has high ratio of syringaldehyde content against vanillin.

Keywords: saccharification reidue, alkaline nitrobenzene oxidation, hydrothermal-mechanochemical pretreatment, autoclave, hydrothermal reaction time

2014-P09

脱メチル化リグニンの構造分析および性質評価

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Synthesis, structure, and antioxidant activity of demethylated lignins

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Abstract: In an attempt to upgrade lignins by augmenting phenolic hydroxyl groups, synthetic lignin (DHP) was treated by demethylation reagents such as 1-dodecanethiol and iodocyclohexane. We found that iodocyclohexane more effectively increased free phenolic hydroxyl groups in DHP than 1-dodecanethiol. Both of the reagents cleaved the side chain linkages prior to demethylation of aromatic methoxyl groups. DPPH radical scavenging activity of the demethylated DHP appeared to be improved as its phenolic hydroxyl content increased.

Keywords: lignin, demethylation, 1-dodecanethiol, iodocyclohexane, antioxidant activity

2014-P10

針葉樹ソーダ蒸解黒液粉末のアルカリ PEG 処理による熱溶融性リグニン誘導体の調製

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Preparation of thermal melting lignin derivatives in the alkaline PEG treatment from dried black liquor powder of softwood soda cooking

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Abstract: Softwood soda lignin does not have thermal melting property. To improve the thermal property of softwood soda lignin, we have invented a new method of lignin modification using dried black liquor powder and polyethylene glycol (PEG). In the process, the black liquor powder of the soda cooking of softwood was directly cooked with PEG in alkaline condition to produce PEG modified lignin derivatives (alkaline PEG treatment). The dried black liquor powder which was prepared by a spray dryer was dissolved into PEG with heating at 120ºC or 160ºC under atmospheric pressure. The modified lignin derivatives (alkaline PEG treated lignin) were precipitated and filtrated out. The collected alkaline PEG treated lignin showed thermal melting property. The chemical analysis data suggested that the number of possible reaction site on lignin with PEG was limited at the treatment of 120ºC. On the other hand, the higher introduction of PEG at the 160ºC of the reaction suggested that the number of the reaction site on the lignin was newly produced by the reaction at 160ºC.

Keywords: thermal melting property; alkaline PEG treatment; softwood soda lignin; dried black liquor powder.

2014-P11

木材腐朽菌によるリグニン分解過程の解析

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Analysis of lignin biodegradation by wood-rotting fungi

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Abstract: Wood biomass is promising resource to produce energy and various chemicals. In nature, wood-rotting fungi is a major player for decompose wood biomass. We have developed several techniques to study wood biodegradation using nuclear magnetic resonance spectroscopy and mass spectroscopy. Selective degradation of either cellulose or lignin depending on a kind of fungi used was successfully detected. A key metabolite for a selective degradation has also been detected with the assist of ^{13}C labeling.

Keywords: basidiomycete, NMR, MS, white-rot fungi, lignocellulose

2014-P12

リグニン分解酵素による硝酸ミコナゾールの分解と毒性除去

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Degradation and detoxification of miconazole nitrate by ligninolytic enzymes

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Abstract: During the last decade, the occurrence and fate of residual pharmaceuticals in wastewater treatment and the environment has attracted increasing interest due to the potential adverse environmental and human health effects. Miconazole nitrate (MCZ) is an imidazole fungicide used for treatment of fungal infections of the skin and vaginal, and is also active against a series of gram-positive bacteria including *Bacillus subtilis*. In this study, MCZ was treated with laccase, the laccase-mediator system with 1-hydroxybenzotriazole, manganese peroxidase (MnP), and the MnP-dependent lipid peroxidation system with Tween 80 containing unsaturated fatty acid. The MnP-Tween 80 system was most effective in eliminating MCZ among the four enzymatic treatments, with MCZ concentration being reduced by about 70 and 88% after 8 and 24 h of treatment, respectively. Furthermore, this system caused the complete loss of growth inhibition of MCZ against *B. subtilis* after 24 h.

Keywords: miconazole; elimination; manganese peroxidase; unsaturated fatty acids; lipid peroxidation

2014-P13

高活性リグニン分解菌 *Phanerochaete sordida* YK-624 株における RNAi 技術の構築

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Gene silencing in hyper lignin-degrading fungus *Phanerochaete sordida* YK-624 by RNA interference

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Abstract: The gene of pyruvate decarboxylase (*pdc*) is a key enzyme in alcohol fermentation. However, lactate dehydrogenase completes with PDC for pyruvate in the lactate production. To produce lactate effectively from woody biomass by hyper lignin-degrading fungus *Phanerochaete sordida* YK-624, the *pdc* was silenced by RNA interference (RNAi). The plasmid constructed for gene silencing contained a transcriptional unit for hairpin RNA expression. The silencing vector was transformed into a *P. sordida* YK-624 uracil auxotrophic mutant, UV-64. When cultivated in fermentation broth for 4 days, 21 of 25 transformants showed lower production of ethanol than control transformant. These results indicated that the silencing of *pdc* is effective for the inhibiton of alcohol fermentation in white-rot fungi.

Keywords: white-rot fungi, biorefinery, alcohol fermentation, RNA interference

2014-P14

Sphingobium sp. SYK-6 株由来の *ligD* 遺伝子を導入した組換えポプラの解析

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Characterization of transgenic poplar with *ligD* gene isolated from *Sphingobium* sp. SYK-6

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Abstract: *Sphingobium* sp. SYK-6, one of gram-negative bacteria, has various enzymes which catalyze the degradation of lignin-related biaryls and monoaryls. One of them, C_α-dehydrogenase, 'LigD', can catalyze the first step of cleavage reactions for ether bonds of β-aryl ether unit which are most abundant bonds in lignin. LigD oxidizes hydroxyl group at benzyl (C_α) position of the dimmers to carbonyl group. It has been known that the presence of carbonyl group at the benzyl position of aryl propane units can greatly improve the efficiency of cleavage of beta-aryl ether linkages during kraft pulping. We introduced the *ligD* gene into plant genome and try to generate transgenic plants whose lignin can be easily to cleave and remove from cell wall fraction under alkali conditions. The enhanced cleavage of β-aryl ether linkages might enable to improve the efficiency not only of pulp and paper production but also of other biorefinery processes. In this study, we generated the *ligD* transgenic poplars and characterization of them will be discussed.

Keywords: SYK-6, LigD, α-keto-β-aryl ether, poplar, biomass pretreatment

2014-P15

遺伝子組換えシロイヌナズナが生産する細菌由来酵素 LigD の局在性の解析

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Imunohistochemical analyses of transgenic *Arabidpsis* plants, which produce the bacterial enzyme LigD.

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Abstract: Bacterial Cα dehydrogenase, which is encoded by *ligD*, catalyzes the first step of cleavage reactions for ether bond of β-O-4-type dimers. This enzyme oxidizes α-hydroxyl group of the dimers to α-carbonyl group. It has been known that the presence of carbonyl group at the benzyl position of β-aryl ether units in lignin greatly speeds up the rate of cleavage of the ether linkage during kraft pulping condition. Hence, we introduced the *ligD* gene into plant genome and try to generate transgenic plants contributed not only to pulp and paper industries but also to efficient biorefinery process. We designed two gene constructs for *ligD* expression in plants under the control of a constitutive promoter. For apoplastic and cytosolic localizations of the LigD protein, *ligD* was expressed with and without an apoplast-targeting signal, respectively. In this study, to test whether LigD with the ATS works as expected, we analyzed LigD localization in transgenic *Arabidopsis* by immunohistochemical analysis and western blotting.

Keywords: dimer, localization, apoplast, immunohistochemical

2014-P16

細菌のリグニン由来芳香族化合物の取り込みに関与する major facilitator superfamily トランスポーター

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Bacterial major facilitator superfamily transporters for lignin-derived aromatic compounds

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Abstract: *Sphingobium* sp. strain SYK-6 is capable of utilizing various lignin-derived aromatic biaryls and monoaryls, and the catabolic genes for these compounds have been characterized. However, the uptake systems for lignin-derived aromatic compounds remained unknown. In this study, we focused on the transporters for protocatechuate (PCA), vanillate, syringate, and ferulate. DNA microarray analyses revealed that the transcriptions of five genes, which probably encode major facilitator superfamily (MFS) transporters, were induced during the incubation of SYK-6 cells on the above-mentioned substrates. These five genes and four other genes homologous to a vanillate transporter gene, *vanK*, of *Acinetobacter* sp. strain ADP1, were disrupted in SYK-6 to determine their roles in the uptake of lignin-derived aromatics. As a result, the growth of a *pcaK* mutant on PCA was delayed compared to that of SYK-6. On the other hand, the *pcaK* mutant grew normally on other substrates. The rate of PCA uptake was significantly decreased in the *pcaK* mutant. These results indicate that *pcaK* encodes an MFS transporter for PCA.

Keywoeds: aromatic acid/H^+ symporter, sequence alignment, complementation assay, Carbon-14, liquid scintillation counter

2014-P17

バクテリア由来コニフェリルアルデヒド二重結合還元酵素の改良

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Improvement of catalytic properties of coniferyl aldehyde double bond reductase

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Abstract: This work aims to control the lignin biosynthesis in plants by using bacterial genes responsible for the structural modification of intermediate metabolites in the monolignol biosynthetic pathway. In a previous study, we focused on alkenal double bond reductases (DBR), which catalyze the reduction of the Cα-Cβ-double bond of coniferyl aldehyde (CALD). We found that DBR of *Parvibaculum lavamentivorans* (PlDBR) showed a higher $V_{\max}$ for the conversion of CALD compared to that of *Arabidopsis thaliana* (AtDBR), whereas the activities of PlDBR were lower than those of AtDBR in the range of low substrate concentration (< 100 □M). In this study, we intended to improve the conversion ability of PlDBR toward CALD. Based on the three-dimensional structure of AtDBR, it was suggested that amino acid residues located in the substrate binding pocket are slightly different between both enzymes. These amino acids of PlDBR were substituted to those of AtDBR, and then the kinetic parameters of mutated PlDBRs to convert CALD were estimated. As a result, a V268I-G269Y mutant showed a 3.5-fold lower K_m value than that of the wild type, indicating an improved substrate affinity, even though the $V_{\max}$ was decreased 0.6-fold over the wild-type value.

Keywords: coniferyl alcohol, biofuel, genome database, site-directed mutagenesis, pretreatment, dehydrogenase

2014-P18

Sphingobium sp. SYK-6 株におけるアセトバニロン代謝経路の同定

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Identification of the acetovanillone catabolism pathway in *Sphingobium* sp. strain SYK-6

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Abstract: Catabolism of arylglycerol-β-aryl ether is the most important process in bacterial lignin catabolism. In a degrader of lignin-derived aromatic compounds, *Sphingobium* sp. strain SYK-6, guaiacylglycerol-β-guaiacyl ether is degraded to vanilloyl acetic acid (VAA) in a five-step reaction. VAA is assumed to be non-enzymatically decarboxylated to produce acetovanillone (AV), and the resulting AV is finally catabolized to vanillate. However, the catabolic pathway of AV to vanillate has not yet been determined. In this study, we characterized the catabolic pathway of AV and identified the catabolism genes. LC-MS analysis showed that VAA was accumulated during the growth of SYK-6 on AV. This result suggests that AV was converted into VAA by carboxylation. The *acvABCDEF* genes specifically induced in the presence of AV were identified as candidate genes responsible for the conversion of AV. Disruption of each of these genes in SYK-6 resulted in a loss of the ability to grow on AV. In addition, the growth on AV of mutants of *ferA* and *ferB* involved in the ferulic acid catabolism were significantly delayed compared to that of the wild type. All these results suggest that *acvABCDEF*, *ferA*, and *ferB* are involved in the catabolism of AV in SYK-6.

Keywords: biomass, bacteria, carboxylase, acetovanillone, ferulic acid

2014-P19

Sphingobium sp. SYK-6 株におけるバニリン酸・シリンガ酸代謝系遺伝子の転写制御機構

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Transcriptional regulation of the vanillate and syringate catabolism genes in *Sphingobium* sp. strain SYK-6

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Abstract: *Sphingobium* sp. strain SYK-6 degrades lignin-derived biaryls via vanillate (VA) and syringate (SA). In this study, we focused on the transcriptional regulation of the VA and SA catabolism genes, including *ligM*, *desA*, and *desB*. To date, it is known that *ligM*, *desA*, and *desB* are negatively regulated by DesR, a MarR-type transcriptional regulator. In order to identify the inducer molecules for the expression of *ligM*, *desA*, and *desB*, the transcriptions of these genes in SYK-6 and a *desA ligM* double mutant (DDAM), which is unable to catabolize VA, SA, and 3-*O*-methylgallate (3MGA), were evaluated by quantitative RT-PCR. When incubating DDAM with VA, SA, or 3MGA, the transcriptional levels of *ligM*, *desA*, and *desB* in DDAM were almost the same as those of the wild type. These results suggest that VA, SA, and 3MGA are inducers of *ligM*, *desA*, and *desB.* Gel shift assays showed that purified DesR bound to the promoter regions of *ligM* and *desB*, each of which contains a similar inverted repeat. However, the binding of DesR to the *desA* promoter region was not observed. Mutations in the inverted repeat in the *desB* promoter region resulted in a reduction of the binding of DesR, suggesting the importance of the inverted repeat for the DesR binding. The binding of DesR to the *ligM* and *desB* promoter regions was inhibited by the addition of VA. This result suggests that VA acts as an effector of DesR.

Keywords: biomass, guaiacyl lignin, syringyl lignin, bacteria, transcriptional regulation

2014-P20

Benzo[a]pyrene biodegradation by a newly isolated white rot fungus from nature in soil

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Abstract: Benzo[a]pyrene (BaP) has been observed to accumulate in marine organisms and plants which could indirectly cause human exposure through food consumption. Bioremediation using white rot fungi is one of the promising method to remove BaP in environment because they can produce extracellular ligninolytic enzymes (Laccase, Mangan Peroxidase, and Lignin Peroxidase) that can degrade many xenobiotic compunds such as BaP. The effect of several pre-grown such as rice straw, wood meal, pulp, kapok, and liquid culture medium was investigated in the degradation of BaP in soil. The fungus could grow in all pre-grown treatment in different cell growth rate. The fungus could cover the surface and bottom part of soil in 7 days incubation. The highest degradation in soil occured in treatment using rice straw as pre-grown, could reach 34.5% in 15 days and 63.2% in 30 days. The degradation varied according to different pregrown media in the range 43.2%-63.2% in 30 days. Ligninolytic enzymes such as laccase. MnP and LiP were detected during incubation. In rice straw treatment, detected laccase, MnP and LiP in order were 63.9 U/L, 11.4 U/L and 38.8 U/L in 15 days. In 30 days, there was MnP decreasing into 1 U/L but enhancement of LiP more than 2 fold, 53.3 U/L. Characteristics of pre-grown biomass such as cellulose, hemicellulose and lignin content seems influence enzyme activity produced by fungus SM46.

Keywords: biodegradation, ligninolytic enzymes, benzo[a]pyrene, fungus SM46

2014-P21

縮合型タンニンを硬化剤とするエポキシ樹脂の合成と熱的性質

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Synthesis and thermal properties of epoxy resins derived from tannin

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Abstract: Epoxy resins were prepared using a fraction of tannin with a relatively low average molecular weight. Tannin, glycerol diglycidyl ether and 2-ethyl-4-methylimidazole (2E4MI) were dissolved in ethanol. Ethanol was removed under a reduce pressure. The obtained mixtures were cured at 130 ºC for 5 h. The [EPOXY]/[PhOH] mole ratios were varied from 0.8 to 1.2. Thermal properties of the obtained cured epoxy resins were studied by differential scanning calorimetry (DSC). The glass transition temperatures (T_g's) showed a maximum value when [EPOXY]/[PhOH] mole ratio was 1.0. The above result suggests that cross-linking densities of the cured epoxy resins become highest when [EPOXY]/[PhOH] mole ratio was 1.0.

Keywords: epoxy resins, tannin, synthesis, thermal properties

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木化に関わるキシランの機能解明

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Clarification of xylan function in lignification

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Abstract: In this study, clarification of xylan function concerning lignification was attempted by using a wood cell wall model mimicking the cell wall formation process. As a result, xylan was found to induce coniferyl alcohol as one of monolignols into inside of the film, and act as a scaffold to form dehydrogenation polymer (DHP). From an analysis of the DHP deposited cellulosic films, xylan was also found to regulate the lignin structure.

Keywords: artificial wood cell wall, immunolabeling, scaffold, SEM-EDXA, xylan,

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免疫賦活作用を持つ大麦穀皮由来リグニン・多糖結合体の発見

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Identification of immune-stimulatory lignin-carbohydrate derived from barley husk

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Abstract: Barley husks are produced as by-products of the malting and brewing industry. In order to develop novel applications of barley husks, biological activities were explored regarding with immune-stimulatory activities. Four lignin-containing fractions were tested using bone-marrow derived dendritic cells (BM-DCs). As a result, LREL and PEL were shown to strongly activate BM-DCs via TLR4. We also examined with the relationship between the immune-stimulatory activity and chemical features of LREL, such as lignin amount, distinguishing composition of neutral sugars and intermolecular ester bonds. In addition, *in vivo* experiments revealed that systemic and mucosal immune systems were significantly activated by LREL administration. Taken together, LREL have shown to be a strong immune-stimulator derived from edible plants.

Keywords: barley husks, lignin-carbohydrate, BM-DCs, immune-stimulatory, TLR4

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ディリジェント様タンパク質の新たな機能の提案：ダイズの莢のねじれへの関わりについて

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Suggestion about a new function of a dirigent-like protein: Relationship to the twist of soybean pods

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Abstract: Pod dehiscence (shattering) is the critical step for seed dispersal in wild plant species, but is a major cause of yield loss in legumes and crucifers crops. However, little is known about the genetic basis of the

shattering resistance in those crops. Here, we performed a map-based cloning of a major quantitative trait locus controlling pod dehiscence in soybean [*Glycine max* Merr. (L.)]. Fine-mapping and complementation test revealed that the gene encodes a dirigent-like protein, which effects stereoselective bimolecular phenoxy radical coupling, designated as Pdh1. The gene was defected with a premature stop codon in shattering-resistant cultivars. The functional *Pdh1* gene was specifically expressed in pod walls. Comparison of near-isogenic lines indicated that Pdh1 regulate torsion of dried pod walls, which functions as force to dehisce binding of pod walls. These findings provide useful information for plant breeding and point to a new biological role for the dirigent proteins.

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シナピルアルコールγ‐アセテートの酸化銀による酸化カップリング

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Oxidative coupling of sinapyl γ-acetate by silver oxide

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Abstract: Biomimetic oxidations of sinapyl alcohol and sinapyl acetate were carried out with Ag_2O to better understand the high frequency of β-O-4 structures in highly acylated natural lignins. The major products from the Ag_2O oxidation of sinapyl alcohol were sinapyl aldehyde (14% yield), β-O-4-coupled dimer (32% yield) and β-β-coupled dimer (3% yield). In contrast, the Ag_2O oxidation of sinapyl acetate produced β-O-4-coupled dimer in 66% yield. Oligomeric products with predominantly β-O-4 structures were also obtained in 18% yield. The yield of the β-O-4-coupled products from sinapyl acetate was much higher than that from sinapyl alcohol. Computational calculations based on density functional theory showed that the negative charge at Cβ was significantly reduced by the γ-acetyl group. The computational calculations suggest that the Coulombic repulsion between Cβ and O4 in sinapyl acetate radicals was significantly reduced by the γ-acetyl group, contributing to the preferential formation of β-O-4 structures from sinapyl acetate. These findings will advance our knowledge in biosynthesis of lignin.

Keywords: monolignol, peroxidase, lignin biosynthesis, acetylated lignin, kenaf

2015-105

二酸化マンガンによるリグニンモデル化合物の酸化反応

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Oxidation of lignin model compounds by manganese dioxide

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Abstract: Manganese dioxide (MnO_2) is a potentially recyclable oxidant. In this study, oxidation reaction of a non-phenolic lignin model compound, veratryl alcohol (I), 2-(2-methoxyphenoxy)-1-(3,4-dimethoxy-phenyl)propane-1,3-diol (II), or 2-(4-hydroxymethyl-2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)- propane-1,3-diol (III), by MnO_2 was examined in detail. The disappearance of compound I became faster with increasing proton concentration of the system, and was relatively accelerated with the progress of the reaction when compared with a pseudo- first-order reaction. Veratraldehyde is the major reaction product of compound I, and the yield was about 80% based on the amount of reacted compound I. Veratraldehyde was also obtained as a major reaction product in the oxidation of compound II, which indicates that the Cα-Cβ bond is cleaved. This result suggests that MnO_2 oxidation can potentially depolymerize lignin. On the other hand, any reaction products resulting from a C-C bond cleavage was not detected in the oxidation of compound III. The presence of the benzyl hydroxymethyl group must have greatly affected the reactivity.

Keyword: manganese dioxide oxidation, permanganate, kappa number, delignification, benzyl alcohol

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リグニンβ-O-4 結合のアルカリ開裂反応における分解生成物の検討

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Study on degradation products in the alkaline cleavage reaction of lignin *β*-O-4 linkage

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Abstract: Based on the mechanism of the non-phenolic *β*-O-4 bond cleavage in alkali medium, alkali cooking of a C_6-C_2 type non-phenolic *β*-O-4 model compound was expected to give a non-phenolic aromatic compound with the 1,2-ethanediol side-chain as the predominant degradation product derived from the main carbon skeleton as well as a phenolic compound liberated from the *β*-O-4 ether linkage. However, the predominant formation of the former compound was observed only when the model compound contained syringyl nuclei in the main carbon skeleton as the 3,4,5-trimethoxyphenyl nuclei. When the model compound containing guaiacyl nuclei in the main carbon skeleton was cooked in alkali, the former compound was only one of the four major degradation products derived from the main carbon skeleton. These were identified as 1-(3,4-dimethoxyphenyl)ethane-1,2-diol, the aimed compound, veratraldehyde, vanillin, and acetoveratrone. The yields of these four degradation products were different when the type of another aromatic nuclei participating in the *β*-O-4 ether linkage was different.

Keywords: alkali pulping, delignification, aromatic ring structure, degradation products

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Stereo-preferential degradation of the *erythro* and *threo* isomers of *β*-O-4 type lignin model compounds under oxygen delignification conditions

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Abstract: The *erythro* (***E***) or *threo* (***T***) isomer of a dimeric non-phenolic *β-O*-4 type lignin model compound, 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (***1***), 2-(4-hydroxymethyl-2-methoxy-phenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (***2***), or 2-(4-methoxymethyl-2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (***3***), was reacted with active oxygen species (AOS) under oxygen delignification conditions to observe the stereo-preferential attack of AOS on the ***E*** or ***T*** isomer. AOS were generated *in situ* by the reaction of O_2 with a co-existing phenolic compound, 4-hydroxy-3-methoxybenzyl alcohol (vanillyl alcohol, Valc system) or 2,4,6-trimethylphenol (TMPh system). When the compound ***1*** or ***3*** was reacted in Valc system, the degradation of ***T*** isomer was greater than that of ***E*** isomer, while compound ***2*** shows the reverse stereo-preference. On the other hand, when the compound ***1*** was reacted in TMPh system, ***1*** isomer was degraded faster than ***T*** isomer. was observed. These results could rationally been explained by the following assumptions. Compound ***1E*** or ***3E*** has the negatively charged *α*-alkoxide owing to the relatively acidic *α*-hydroxy group, and consequently, is not frequently attacked by the negatively charged AOS, oxyl anion radical, in Valc system. On the other hand, because the neutral peroxyl radical is a main AOS in TMPh system, the negatively charged side-chain of compound ***1E*** or ***3E*** can be attacked. In compound ***2***, the presence of the more easily ionizable benzyl hydroxymethyl group may suppress the ionization of the *α*-hydroxy group of ***2E***, and hence the reaction of the main carbon skeleton with the negatively charged oxyl anion radical may not be interfered with.

Keyword: Alkyl-aryl ether, bleaching, diastereomers, pulp, oxidation

2015-108

砕木パルプのアセチル化 —アセチル基の導入量と導入位置の関係—

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Acetylation of ground pulp –the quantity and the position of acetyl groups-

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Abstract: In acetylation of ground pulp(GP), the position of Acetyl groups was researched. Seven different AcGPs (DS=0.19,0.29,0.59,0.74,1.04,1.11,1.19) were prepared and analyzed with HSQC-NMR. Acetylation was proceeded in the order of primary hydroxyl groups of polysaccharide and lignin, secondary hydroxyl groups of polysaccharide, and hydroxyl groups at α-position of lignin. Then, the thermal stability of the AcGPs was analyzed with TGA. The 1%loss temperatures of AcGPs were higher than GP. Especially, it was found that acetylation of primary hydroxyl groups and hydroxyl groups at α-position of lignin improved the thermal stability.

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高活性リグニン分解菌 *Phanerochaete sordida* YK-624 株と自然界由来細菌の共培養系の構築

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Construction of co-culture system of hyper lignin-degrading fungus *Phanerochaete sordida* YK-624 with the naturally derived bacteria that indicated the higher ligninolytic activity

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Abstract: To investigate the interaction between wood rot fungi and bacteria in nature wood decay, we tried to construct a wood rot fungal-bacterial coexisting culture system showing higher wood degrading ability. Fungal cultures on beech wood meal of *Phanerochaete sordida* YK-624 were buried in soils for 1 to 5 weeks. The resulting cultures have been contaminated by soil bacteria. Subcultures of contaminated-cultures to the newly wood meal have shown higher wood degrading rate than *P. sordida* YK-624. The contents of residual wood components of each subcultures were different. Therefore, it is suggested that the coexisting bacteria affected wood degradation mechanisms of wood-rotting fungus *P. sordida* YK-624. Moreover, the results of bacterial ribosomal intergenic sequence analysis showed progression of bacterial diversity change and stabilization by repeating subcultivation.

Keywords: white-rot fungi, wood rot, co-culture, interaction

2015-110

担子菌を用いた木質バイオリファイナリーの新展開　－白色腐朽菌による水素発酵－

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New development on woody biorefinery with basidiomycete - Hydrogen fermentation by white-rot fungi-

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Abstract: Hydrogen is potential alternative pollution-free energy carrier. In nature, hydrogen is produced by microorganisms either in the process of nitrogen fixation, fermentative processes or by photosynthetic microorganisms under certain conditions. It is known that fermentative hydrogen production by anaerobic bacteria, for example, *Clostridium* and *Enterobacter*. Although we confirmed the presence of hydrogenase-like gene sequence in many wood rotting fungi, there are no repodescribed on hydrogen production by wood-rotting fungi. In the present study, we investigated the possibility of hydrogen production by wood-rotting fungi. We selected 3 hydrogen-production fungi from 26 wood-rotting fungi isolated from decay woods, and confirmed that they were white-rot fungi. Quantitative determination of hydrogen production by these white-rot fungi was performed by using gas chromatography. As a result, *Trametes versicolor* K-41 showed the highest hydrogen producing ability, and we expected that the expression of hydrogenase gene in *T. versicolor* K-41 was involved in the hydrogen production. Furthermore, it was indicated that *T. versicolor* K-41 could produce the hydrogen from Japanese cedar wood meal. This is the first report of hydrogen production from wood biomass by white-rot fungus.

Keywords: wood-rot fungi ; hydrogen fermentation ; hydrogenase gene ; *Trametes versicolor* K-41

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シロイヌナズナゲノムに存在するフェニルクマランベンジルエーテルレダクターゼ遺伝子の機能解析

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Expression and functional analyses of a putative phenylcoumaran benzylic ether reductase in *Arabidopsis thaliana*

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Abstract: Phenylcoumaran benzylic ether reductase (PCBER) is thought to be an enzyme crucial in the biosynthesis of 8–5′-linked neolignans and have been characterized in several plant species. Interestingly, in poplar, expression of *PCBER* is strongly correlated with active xylem formation. In this study, we cloned cDNA and the 5′-untranslated region of a PCBER candidate gene (*At4g39230*, designated as *AtPCBER1*) from *Arabidopsis thaliana*. Expression analyses of *AtPCBER1* indicate that expression is induced by wounding and is expressed in most of tissues, including flower, stem, leaf, and root. Catalytic analysis of recombinant AtPCBER1 suggests that the protein can reduce not only the 8–5′-linked neolignan, dehydrodiconiferyl alcohol, apparently but also 8–8′ linked lignans, pinoresinol, and lariciresinol with lower activities. Untargeted metabolomics analysis of transgenic plants in which the target gene was up- or down-regulated indicates no hsignificant effects of *AtPCBER1* gene regulation on plant growth and development, however, levels of some secondary metabolites, including lignans, flavonoids, and glucosinolates, differ between wild-type and transgenic plants. Taken together, our findings indicate that *AtPCBER1* encodes a polypeptide with PCBER activity and has a critical role in the biosynthesis of secondary metabolites in *A. thaliana*.

Keywords: *Arabidopsis thaliana*, Dehydrodiconiferyl alcohol, Lignan, Metabolome

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フェルラ酸 5-ヒドロキシラーゼ *OsF5H1* の発現制御によるイネリグニンの構造改変

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Structural modification of lignin in *Oryza sativa* by regulation of *ferulate 5-hydroxylase* (*OsF5H1)* expression

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Abstract: Lignin aromatic composition, i.e., syringyl (S) and guaiacyl (G) unit ratio, greatly affects the usability and processability of lignocellulosic biomass. In this study, we attempted to control S/G lignin unit ratio in rice (*Oryza sativa*), a model plant of grasses, by manipulation of a gene encoding ferulate 5-hydroxylase (F5H; a.k.a, coniferaldehyde 5-hydroxylase, CAld5H). Based on protein sequence and gene expression data analysis, we identified a candidate gene (*OsF5H1*) for the primary F5H involved in S lignin biosynthesis in rice. Accordingly, we produced transgenic plants in which *OsF5H1* is down- or up-regulated, and demonstrated that their lignins are considerably enriched in either S or G lignin units as determined by a series of chemical and spectroscopic analyses. We contemplate that manipulation of F5H genes could be a promising strategy to improve the utilization of grass lignocelluloses.

Keywords: lignin, rice, ferulate 5-hydroxylase, S/G ratio, metabolic engineering

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バクテリア由来 Cα-デヒドロゲナーゼの発現による細胞壁中でのリグニンの構造改変

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Structural modification of lignin in the cell wall by the use of bacterial Cα-dehydrogenase

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Abstract: *Sphingobium* sp. strain SYK-6 can utilize various monomeric and dimeric aromatic compounds, which appeared in lignin biosynthetic pathway. In our previous study, some genes involved in degradation of these compounds were isolated from this strain. One of them, *ligD* gene, encodes Cα-dehydrogenase for first step of cleavage of ether bond in compounds with β-O-4 bond. It has been known that the presence of carbonyl group at the benzyl position of β-O-4 interunits in lignin accelerates up the rate of cleavage of the bond during alkaline and acidic conditions. Thus, we introduced the *ligD* genes into plant genome and try to generate transgenic plants. Characteristics of the transgenic *Arabidopsis*, *Populus* and *Eucalyptus* plants will be discussed in the present study.

Keywords: *Sphingobium* sp. strain SYK-6, Cα-dehydrogenase, ^{1}H-^{13}C HSQC analysis, apoplast-targeting signal (ATS)

2015 特別講演、I.

リグニンの微生物分解

片山 義博
日本大学 生物資源科学部

Ivited Lecture, I : Microbial degradation of Lignin

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Abstract: In microbial degradation process in nature, bacteria play a main role in the mineralization of various types of lignin-derived aromatic compounds. *Sphingobium* sp strain SYK-6 grows on a lignin-related biphenyl compounds, 5,5'-dehydrodivanillate (DDVA), as sole carbon and energy sources and also degrades various types of lignin-derived biaryls, including β-aryl ether, pionresinol, phenylcoumaran and diarylpropan together with DDVA. These versatile degradation activities toward various types of lignin-related compounds reflect the presence of a wide variety of enzyme systems in this bacterium. We have been investigated the enzyme and gene systems for β-aryl ether cleavage by two enantioselective enzymes (LigE, F), two types of O-dimethylation for DDVA by mono-oxygenase (LigX) and for vanillate and syringate by methyl-transferase linked with C1-metabolism (LigM), two types of aromatic ring cleavage for biphenyl derived from DDVA(LigZ) and for protocatechuate and 3-methylgallate derived from vanillate and syringate, respectively (LigA,B). For applications, we focused on the metabolic intermediate, 2-pyrone-4.6-dicarboxylic acid (PDC) as a potential raw material for variuous novel bio-based polymers. We established the preparation protocol of a PDC, on a large scale from lignin using transformed bacterium by combination with chemical reaction as pretreatment of high molecular lignin decomposition. PDC a chemically stable metabolic intermediate of lignin, was utilized to prepare polyesters. PDC polyesters and PDC epoxides exhibited strong adhering properties against metals and glass with tenaciously adhering to their surface

Keywords: Glutathione S-transferase, Lignin biphenyl ring cleavage, Lignin biphenyl *O*-demethylation, Tetrahydrofolate-dependent *O*-demethylation, PDC-based polymer, PDC-based Adhesive

2015-201

オゾン処理が針葉樹ソーダリグニン系のコンクリート用化学混和剤の性能に与える効果

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Effect of ozone treatment on performance of softwood soda lignin based concrete chemical admixture

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Abstract: We have developed a water reducing admixture for concrete based on softwood soda lignin modified with polyethylene glycol (PEG) chain. In this study, ozone treatment of soda lignin and lignin-PEG derivatives was conducted in order to introduce carboxyl group which can be responsible for adsorpting to surface of cement particles for developing a high performance of lignin based water reducing admixture. Ozone treatment of soda lignin increased the number of free type of carboxyl group and improved mortar fluidity. The lignin-PEG derivatives having various amount of PEG moiety (50 and 90 mol of ethylene oxide repeating unit) were prepared and applied to ozone treatment as well. Ozone treated lignin-PEG derivatives showed better performance as water reducing admixture than untreated samples. This effect should be due to introducing carboxyl group which work as adsorpting site to cement particles.

Keywords: soda lignin, Japanese cedar, polyethylene glycol, ozone treatment, concrete chemical admixture

2015-202

数種の単離リグニンからの電気二重層用電極の調製

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Preparation of electric double layer capacitor electrode from several kinds of isolated lignins

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Abstract: In this study, fabrication of electric double layer capacitor (EDLC) electrode was attempted by using polyethylene glycol-lignin (PEGL) and soda-lignin (SL) derived from cedar wood. By direct melt-electrospinning of PEGL, fibers with 23 μm in diameter were prepared. Much finer fibers (3.6 μm) were obtained by melt-electrospinning of 70% PEGL in dimethyl formamide (DMF) solution. Although dry-electrospinning of SL alone in an alkaline aqueous solution was impossible, dry-electrospinning of a mixture of SL and polyethylene glycol (M_w=500,000) was possible to give thin SL fibers with the diameter of 0.85 μm. These fibers were converted to activated carbon fibers (ACFs) by stabilization, carbonization and steam-activation as the EDLC electrode materials. By using these carbonaceous materials, PEGL-ACF electrode showed an impedance of 1.6 Ω and a specific capacitance of 92.6 F g^{-1} at a scan rate of 1 A g^{-1}, and SL-ACF electrode showed 4.5 Ω and 55.6 F g^{-1}, respectively.

Keywords: dry-electrospinning, electric double layer capacitor, melt-electrospinning, polyethylene glycol lignin, soda lignin

2015-203

リグニン由来の新規難燃材料の開発

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Development of novel flame retardant from by-product lignin in pulping process

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Abstract: Nitrogen-phosphorus-alkyldiol modified Lignin (NPDL) was prepared from kraft lignin. The procedure was introduction of 3-amino-1,2,4-triazole into kraft lignin and phosphorylation using phosphoryl chloride followed by introduction of 8-octanediol. NPDL and poly(lactic acid)-NPDL composite (PLA-NPDL) were investigated thermal stability and flame retardancy. NPDL exhibited char-forming ability with retaining 44.9 wt% mass at 500 ºC in atmosphere. PLA-NPDL composite was achieved V-2 class in UL-94 test. The char layer was formed on NPDL surface in simplified combustion test. Moreover, NPDL did not drip flaming particles. NPDL exhibited high flame retardancy with growing intumescent char layer.

Keywords: industrial lignin, functionalization, resinification, additive, biorefinery

2015-204

ブナの亜臨界フェノール及び亜臨界水による脱リグニンの比較

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Comparative study of delignification from Japanese beech as treated by subcritical phenol and subcritical water

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Abstract: The difference in delignification behaviors of Japanese beech (*Fagus crenata*) was discussed as treated by subcritical phenol (230ºC/1.2MPa) and subcritical water (230ºC/2.9MPa). As a result, in subcritical phenol, more than 90 wt% of lignin was decomposed and removed, while in subcritical water, around half of lignin was removed with the other half remaining as insoluble residue. Through the ultraviolet (UV) microscopic observations, lignin in cell walls was found to be decomposed extensively in both treatments due perhaps to ether-linkages rich in cell wall lignin. However, lignin in middle lamella revealed resistance to subcritical water, but not to subcritical phenol. Such a difference would imply that the lignin is phenolated and simultaneously decomposed in subcritical phenol. The phenolated lignin would, thus, become solvated with phenol. Consequently, lignin in middle lamella, even being rich in condensed-type linkages, would be more liquefied by subcritical phenol, compared to subcritical water.

Keywords: Topochemistry, Japanese beech, Subcritical phenol, Subcritical water, Microscopy

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2015-205

リグニン熱分解における芳香核構造の変換機構 —同位体ラベルによる検討—

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Conversion mechanisms of aromatic nuclei during lignin pyrolysis – An approach from isotope labeling –

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Abstract: Structures of lignin aromatic nuclei dramatically change at > 400-450ºC, where the methoxyl groups become reactive. In this study, conversion mechanisms of the aromatic nuclei during pyrolysis were studied from the reactivity and ^{13}C/deuterium (D) incorporation data with ^{13}C and D labeled guaiacols as model compounds.

Keywords: lignin, pyrolysis, polyaromatization, methoxyl group, isotope labeling

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2015-206

イオン液体処理におけるMWLの分解挙動の解析

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Ultrastructural and Topochemical Aspects of Wood Cell Walls Treated with Ionic Liquid

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Abstract: We investigated for the reaction behavior of milled wood lignin (MWL) obtained from Japanese cedar (*Cryptomeria japonica*) and Japanese beech (*Fagus crenata*) in an ionic liquid, 1-ethyl-3-methylimidazolium chloride ([C2mim][Cl]), which is known that it can liquefy wood and dissolve cellulose. Both MWLs easily dissolved in [C2mim][Cl] heated at 120℃ by oil bath and microwave irradiation. After 96h treatment with [C2mim][Cl], MWLs were slightly depolymerized. Few amount of low molecular weight compounds such as vanillin and coniferylaldehyde were produced from MWL. Moreover, the reaction behavior of MWL in 1-ethyl-3-methylimidazolium aminoacetate ([C2mim]Gly) and tetrabutylammonium hydroxide 30-hydrate ([NBu4]OH) were also studied. [C2mim]Gly and [NBu4]OH can dissolve MWL during heat treatment. The solubilized MWL in these ionic liquids were depolymerized much faster than that in

[C2mim][Cl].

Keywords: Ionic liquid, Milled wood lignin, Reaction, Depolymerization

2015-207

イオン液体を移動相とする HPLC：イオン液体でバイオマスから抽出したリグニン・多糖類の分子量分布測定

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Molecular weight distributions of polysaccharides and lignin extracted from plant biomass with a polar ionic liquid analyzed without a derivatization process

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Abstract; Lignin and polysaccharides, extracted from biomass with ionic liquids, were directly analyzed with high performance liquid chromatography with the aid of ionic liquid as an eluent(HPILC). Lignin and polysaccharides and were clearly detected independently with the use of both a refractive index detector and UV detector. The present HPILC method has potential to rapidly and easily analyze molecular weight distributions of lignin and polysaccharides extracted from plants.

Keywords: molecular weight distribution, HPLC, GPC, ionic liquid, lignin-carbohydrate complex

2015-特別講演、II.

Invited Lecture II: Designer lignins

John Ralph,[1,2]* Fachuang Lu,[1,2] Hoon Kim,[1,2] Steven D. Karlen,[2] Matt Regner,[1,2] Dharshana Padmakshan,[2] Rebecca Smith,[1,2] Yuki Tobimatsu,[1,2,*] Wu Lan,[1,2] Jorge Rencoret,[2,†] Kate E. Helmich,[1,2] Sally A. Ralph,[3] John C. Sedbrook,[2,4] Curtis G. Wilkerson,[5] Philip J. Harris,[6] Armin Wagner,[7] John H. Grabber,[8] Ronald D. Hatfield,[8] Jane Marita,[8] Yukiko Tsuji,[1,9] Shinya Kajita,[9] Yaseen Mottiar,[10] Shawn D. Mansfield,[2,10] and others!

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Abstract: As lignin is a polymer formed from its monomer radicals by purely chemical radical coupling reactions, the breadth of options for ‘designing’ the composition and structure of lignins is unparalleled. Beyond simply manipulating the relative levels of the traditional monolignols, new phenolic monomers can be introduced into the polymer, subject solely to the plant’s ability to produce and transport them to the wall and their chemical compatibility with the components and (cross-)coupling reactions that typify lignification. Recent examples of this metabolic plasticity include demonstrating the introduction of hardwood-type lignins into soft-woods to improve pulping performance, and the identification of plants producing lignins composed almost entirely of hydroxycinnamaldehydes, opening up new and unique derivatization and modification opportunities. Tissues containing 100% levels of caffeyl or 5-hydroxyconiferyl alcohol-derived lignin polymers have been discovered. These two catechol-type monolignol analogs produce almost homogeneous (single-structured) linear lignin chains upon polymerization, again creating opportunities for valuable new uses for lignin. Moreover, lignins have now been successfully ‘redesigned’ to contain readily chemically cleavable ester bonds in the polymer backbone, facilitating improved industrial processing – for example, chemical pulping, or pretreatment options for the saccharification of wall polysaccharides to sugars for liquid biofuels production. Inspired by Nature’s incorporation of the non-lignin-pathway flavonoid, tricin, into monocot lignins, researchers can now also contemplate plants in which the lignins incorporate valuable components that can be subsequently retrieved from the 'waste' streams. We suspect that we are now entering a reinvigoration period for lignin research aimed at its manipulation for improved utilization, and suggest that the title 'designer lignins' used here is not overly hyperbolic!

Keywords: Lignification, metabolic plasticity, monolignol, gene misregulation, engineering, pulping.

2015-P01

広葉樹の葉リグニンの DFRC 法による検出（２）

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Detection of broad-leaf lignin in angiosperms by DFRC analysis (2)

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Abstract: The DFRC (**D**erivatization **F**ollowed by **R**eductive **C**leavage) analysis can be used to detect lignin specifically from plant tissues, since it gives C6-C3 type degradation products by the cleavage of arylether linkages of lignin, excluding other (poly)phenolic substances. In this study, the process of lignin deposition in the course of leaf growth was investigated by DFRC analysis. The increase of lignin in leaves of *Fagus*, *Magnolia* and *Cercidiphyllum* was observed from late April to mid May. Localization of lignin in major leaf vein was not clear, but there was heterogeneity in the lignin composition between major leaf veins and other leaf tissues. Vein lignin showed clearly low S/G ratio.

Keywords: lignin, leaf, DFRC method, vein

2015-P02

合成モノリグノールプローブを活用した細胞壁リグニンの蛍光生体標識

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Visualization of Cell Wall Liginification Using Synthetic Monolignol Probes

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Abstract: Techniques to visualize cell wall lignification processes directly *in vivo* are considerably limited mainly because lignins are not amenable to being genetically tagged for visualization. To overcome this, we have developed a series of synthetic monolignol analogues imbued with chemical reporters (e.g., azides and alkynes) that can be selectively incorporated into lignin-producing cell walls and subsequently derivatized via bioorthogonal reactions (e.g., click chemistry) for fluorescent labeling. Herein, using Arabidopsis live plant systems, we have further explored the use of azide- and alkyne-tagged monolignol probes and various fluorescent dyes for *in vivo* fluorescent imaging of cell wall lignins via copper-assisted or copper-free click reactions.

Keywords: *Arabidopsis thaliana*; azide-alkyne cycloaddition reaction; fluorescence microscopy; *in vivo* imaging; lignin biosynthesis

2015-P03

β–1 型構造に関する研究：塩酸処理による MWL の NMR スペクトル変化

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Study on β–1 structures in lignin:
NMR spectral changes of MWL during hydrochloric acid treatment

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Abstract: Hardwood lignin (MWL) was treated with 0.1M hydrochloric acid in dioxane-water (80:20, v/v) at 50ºC. After the acid treatment, candidate NMR signals for spirodienone structures (β–1) almost disappeared from the HSQC spectrum of the MWL. In contrast, a NMR signal for the β-position of diarylpropane structures became detectable in the course of the acid treatment.

Keywords: acidolysis, milled wood lignin, β-1 linkage, guaiacyl-syringyl, avicennia

2015-P04

バイオマス生産現場への導入を目指した改質リグニン製造用ベンチプラント

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国立研究開発法人 森林総合研究所

Local type of bio-refinery plant development to produce functional lignin derivatives

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Abstract: Recently, FFPRI lignin research has been upgraded by a large scale national research program of Strategic Innovation promotion Program (SIP) under the direction of Council of Science Technology and Innovation, Cabinet Office, Government of Japan. To start this new lignin program, 22 organizations (5 national laboratories, 9 universities and 8 private companies) participated and launched a new research consortium called "SIP-Lignin". In the SIP-Lignin project, acid catalyzed solvolysis of wood meal with PEG (PEG solvolysis) was selected as a main biorefinery process. Since PEG is a not toxic high boiling point solvent, the PEG solvolysis reactor can be operated under atmospheric pressure without using pressure equipment. This simple operability brought a concept of introducing a small scale rural area biorefinery system based on the PEG solvolysis. A bench scale plant has been introduced to demonstrate the concept with a stable PEG lignin production.

Keywords: solvolysis, PEG, bench scale plant, bio-refinery, SIP-Lignin

2015-P05

酸加溶媒分解による改質リグニン製造工程からの薬液の回収と再利用

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Recovery and reuse of the solvolysis reagent in the acidic solvolysis system of the glycol lignin production

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Abstract: The acidic solvolysis of softwood with a glycol solvent, such as polyethylene glycol (PEG), is considered to be an attractive way to produce a valuable lignin with thermal fusibility. In order to industrialize this process, a solvolysis reagent need to be recovered and reused. In this study, the recovered PEG200 was prepared by removing water from the waste liquor of the acidic solvolysis system of the glycol lignin production, and then was used in the acidic solvolysis reaction of softwood. The recovered PEG200 worked as a solvolysis media and produced the glycol lignin with thermal fusibility. Thermomechanical analysis of the glycol lignin in 2.0 h of the reaction showed that both of fresh and the recovered PEG200 displayed two inflection points, which were assigned to the glass transition point (Tg) and the thermal softening point (Ts).

Keywords: recycle of solvolysis reagent, acidic solvolysis, glycol lignin, polyethylene glycol (PEG), softwood

2015-P06

Thermal flow behavior of isolated softwood lignin derivatives depending on polyethylene glycol (PEG) chain length using as a solvolysis medium

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Abstract: The acid catalyzed solvolysis of softwood Japanese cedar was performed using liquid polyethylene glycol (PEG) with different PEG chain length as solvolysis medium. The physical and thermal properties of isolated PEG-lignin derivatives obtained from PEG solvolysis medium (PEG200, PEG400, PEG600) with substantial amount of acid catalyst concentration (0.3 to 0.7% w/w% of PEG) were then investigated by UV spectrophotometer, size exclusion chromatography, and various thermal analyzers including TMA, TGA, CFT (Capillary Flow Tester Rheometer). It was noted that an efficient separation of PEG-lignin fraction and lignocellulosic pulp fraction can be performed with this single step solvolysis process. A comprehensive thermal flow profile of PEG-lignin derivatives was deduced from combination of thermal analyses results.

Keywords: acid catalyzed solvolysis, polyethylene glycol (PEG), thermal flow behavior, capillary flow tester rheometer (CFT), thermomechanical analyzer (TMA)

2015-P07

Characterization of lignin in residual pulp fraction obtained from polyethylene glycol solvolysis of softwood Japanese cedar by pyrolysis gas chromatography mass spectrometry

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Abstract: The acid catalyzed solvolysis of softwood Japanese cedar was carried out using polyethylene glycol (PEG) as a solvolysis reagent in the presence of a very small amount of sulfuric acid (H_2SO_4) to isolate lignin fraction. The lignin remained in the residual pulp fraction obtained from solvolysis process were then analyzed by the pyrolysis gas chromatography mass spectrometry (Py-GC/MS) in comparison with a starting material of Japanese cedar. In order to estimate the lignin contents in residual pulp fraction, a calibration line was developed based on Py-GC/MS results of residue with various lignin contents, which were first determined by Klason and UV method. It was noted that the lignin contents (Klason lignin and acid soluble lignin) was in good agreement with that measured by Py-GC/MS.

2015-P08

リグニンと粘土鉱物を用いた耐熱ガスバリアフィルムの開発

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Abstract: 我々は、粘土鉱物を主体とした耐熱ガスバリアフィルムの開発を行っている。当該バリアフィルムは粘土を主成分としているため、その強度が弱く、有機バインダーを使用することにより膜の形態を保持している。さらに、そのバインダーの特性はフィルムの耐熱性やバリア性に影響を及ぼすことが分かっており、バインダーの選択はフィルムの性能向上に重要な要素となっている。今回、有機バインダーとして熱的な安定性が期待されるリグニンに注目し、リグニンと粘土鉱物を用いた耐熱ガスバリアフィルムを試作し、その評価を行ったので報告する。

2015-P09

改質リグニンに反応性基導入による硬化

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Thermal Curing of a Glycol Lignin by the Introduction of Reactive Groups

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Abstract: Hybrid materials composed of clay and glycol lignin make flexible films with high gas-barrier ability, high resistance against electric discharge, and thermal stability. In order to improve the mechanical properties of those hybrid materials introduction of reactive groups on the glycol lignin was investigated to perform thermal curing of the films. Phenolic hydroxyl groups and the hydroxyl groups of ethylene glycol chains on the glycol lignin were determined as 1.89mmol/g and 2.35mmol/g, respectively based on the acetylation method. Then several functional groups such as diisocyanates, dianhydrides, chlorides, epoxides and so on were introduced on the active hydroxyl moieties to harden the materials. Among them introduction of (di)anhydrides was especially effective to the fabrication process due to water-solubility of the modified glycol lignin and reactivity towards to poycarbodiimides. This work was supported by SIP-Lignin project, "Technologies for creating next-generation agriculture forestry and fisheries" Cross-ministerial Strategic

Innovation Promotion Program (SIP), Council for Science Technology and Innovation (CSTI).
Keywords: glycol lignin, hybrid film, clay, curing

2015-P10

アルカリ PEG 処理による針葉樹ソーダリグニンの改質と特性解明

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Improvement and characterization of softwood soda Lignin in the alkaline PEG treatment

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Abstract: To develop applications for technical lignins, it is important to develop modification methods to enhance lignin properties for high-end value-added products. We prepared lignin derivatives by using dried black liquor powder with polyethylene glycol (PEG). In the process, the black liquor powder of the soda cooking of softwood was directly cooked with PEG in alkaline condition to produce PEG modified lignin derivatives (alkaline PEG treatment). The lignin derivatives showed thermal melting property. To elucidate the behavior of lignin in this treatment, we carried out the alkaline PEG treatment using the purified soda-AQ lignin as model compound. In this paper, the molecular weight of alkaline PEG-treated lignin and evaluation of thermal melting property will be discussed.

Keywords: softwood soda-AQ lignin, polyethylene glycol, alkaline PEG treatment, thermal melting property, black liquor

2015-P11

シリンギル構造を有するビフェノールを硬化剤とするエポキシ樹脂硬化物の合成と熱的性質

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Synthesis and thermal properties of epoxy resins derived from biphenol having syringyl groups

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Abstract: Epoxy resins were prepared by curing with 4,4’-dihydroxy-3,3’5,5’-tetramethoxybiphenyl (DHTMB) and 4,4’-dihydroxybiphenyl (DHB) in the presence of 2-ethyl-4-methylimidazole (2E4MI). The mixture of ethylene glycol diglycidyl ether (EGDGE) and trimethyrol propane triglycidyl ether (TMPTGE) were allowed to react with the above biphnols at 120 °C, in order to obtain prepolymers. The obtained prepolymers were cured by heating from 20 to 200 °C in vessels using a differential scanning calorimeter (DSC). The [EPOXY]/[PhOH] mole ratio was maintained at 1.0. Thermal properties of the obtained cured epoxy resins were studied by DSC. The glass transition temperatures (T_g’s) of cured epoxy resins with DHTMB was 46.4 °C and that of DHB was 38.8 °C. The above result suggests that methoxyl groups in DHTMB units restricts the main chain motion of cured epoxy polymer networks
Keywords: biphenol, syringyl groups, epoxy resins, synthesis, thermal properties

2015-P12

tetra-*n*-butylphosphonium hydroxide を用いた針葉樹リグニンの抽出

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Extraction of softwood lignin using a tetra-*n*-butylphosphonium hydroxide

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Abstract: Tetra-*n*-butylphosphonium hydroxide ($[P_{4,4,4,4}]OH$) is a kind of ionic liquids. $[P_{4,4,4,4}]OH$ can dissolve micro crystalline cellulose and hardwood biomass at ambient temperature, even when it contains 30~70% of water. In this study, the dissolving properties of softwood lignin in an aqueous solution of $[P_{4,4,4,4}]OH$ were studied. Cedar wood meal and 40% $[P_{4,4,4,4}]OH$ aqueous solution were mixed in a glass tube and treated at 121 °C and 2 atm in an ordinary autoclave. As the treatment time increased, the residue content

decreased to 68.7%, 49.4%, and 37.0% after 1, 5, and 20 h, respectively. Lignin was found to dissolve faster than holocellulose, and 3.0% of the residue after the 20-h autoclave treatment consisted of lignin. In that residue, glucose was the main constituent monosaccharide (96.3%). The dissolved lignin content in the [$P_{4,4,4,4}$]OH solution could be determined by UV analysis. The lignin absorption coefficients can be proposed as 39.5 L/g/cm, calculated from the lignin elution amount and the 280nm UV absorbance. Phenolic hydroxyl group of the dissolved lignin were 0.43-0.49 mol/unit lignin, indicating that the treatment time did not affect the phenolic hydroxyl content.

Keywords: ionic liquid, TBPH, cedar, dissolution, autoclave

2015-P-13

イオン液体処理木材の組織形態および化学成分変化のトポケミストリー

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Ultrastructural and topochemical aspects of wood cell walls treated with ionic liquid

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Abstract: We have studied the morphological and chemical changes in cell walls of Japanese beech (*Fagus crenata*) after treatment with the ionic liquid, 1-ethylpyridinium bromide ([EtPy][Br]), which prefer to react with lignin to cellulose. The cell walls of wood fibers in both earlywood and latewood were significantly swelled after [EtPy][Br] treatment. In addition, lignin in compound middle lamella and cell corner have high resistance to degradation by [EtPy][Br] compared with that in secondary wall.

Keywords: ionic liquid, liquefaction, microscopy, morphology, topochemistry

2015-P14

有機分子触媒能を持つイオン液体を用いたリグニンの誘導体化

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Synthesis of lignin derivatives by using organocatalyst in ionic liquid

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Abstract: Lignin is a major component of biomass, abundant in nature and the resource for aromatic compounds. Therefore, converting lignin into a useful substance is one of the most important processes in biorefinery. However, lignin has not been employed as a chemical resource because lignin shows structural complexity, poor reactivity and solubility in organic solvents. We focus on ionic liquid as solvent to realize facile reaction of lignin. Ionic liquid featuring basic anion such as 1-Ethyl-3-methylimidazolium acetate (EmimOAc) generates *N*-heterocyclic carbenes (NHCs) and works as organocatalyst 1). In this study, lignin was modified by using EmimOAc as solvent and catalyst to transform raw lignins into acetylated lignin.

Keyword: ionic liquid, organocatalyst, carbenes, transesterification, hydroxyls

2015-P15

Effect of activated carbon on impurities removal of recycled [Emim]Ac (1-Ethyl-3-Methyl- imidazolium Acetate) for enzymatic saccharification

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Abstractionic liquids pretreatment with [Emim]Ac (1-ethyl-3-methylimidazolium acetate) was carried out for enzymatic saccharification to produce glucose from cellulose in Japanese softwood, *Cryptomeria japonica.* Recycling process of [Emim]Ac was conducted by mixing the activated carbon into filtrate which containing [Emim]Ac to remove impurities from filtrate. Visually, activated carbon treatment could successfully eliminate the black color of recycled [Emim]Ac, whereas *n*-hexane & ethanol treatment could not. After the enzymatic saccharification of wood meal treated with [Emim]Ac, the yield of liberated glucose was 10.8% for the recycling with activated carbon, slightly higher than without the activated carbon treatment (9.4%). However, this value was still lower than using fresh [Emim]Ac which could produce 36.2 % of glucose.

2015-P16

海洋性 *Novosphingobium* 属細菌に由来するリグニンモデル 2 量体 β-*O*-4 結合開裂酵素群の酵素学的解析

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Kinetic study of the β-*O*-4 cleaving enzymes of a marine *Novosphingobium*

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Abstract: Bacterial enzymatic cascade for β-*O*-4 reductive cleavage in lignin model dimers consists of short-chain dehydrogenase/reductases (SDRs), β-etherases and β-glutathione thioetherases (glutathione lyase). We previously isolated a marine *Novosphingobium* from a sunken wood, detected β-*O*-4 cleavage activity and determined the responsible genes for the activity. In this study, we conducted kinetic study of the enzymes to understand fundamental properties of the enzymes. Furthermore, a structural model of a SDR was constructed to discuss the structure-function relationship of the enzyme belonging SDR super family which holds versatile activities.

Keywords; marine *Novosphingobium,* β-*O*-4 reductive cleavage, short-chain, dehydrogenase/reductase, β-etherases, β-glutathione thioetherase, glutathione lyase

2015-P17

リグニンモデル 2 量体中 β-*O*-4 結合を開裂する海洋性 *Novosphingobium* 属細菌のゲノムおよびトランスクリプトーム解析

西　真郎、黒澤佳奈子、小林樹和、坪内泰志、秦田勇二、大田ゆかり

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Genome and transcriptome analyses of a marine *Novosphingobium* capable of cleaving the β-*O*-4 linkage in the lignin model dimer

Shinro Nishi, Kanako Kurosawa, Kiwa Kobayashi, Taishi Tsubouchi, Yuji Hatada, Yukari Ohta

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Abstract: We previously isolated a marine *Novosphingobium* from a sunken wood and detected β-*O*-4 cleavage activity of the isolate. In this study, we carried out genome and transcriptome analyses to understand the environmental response to lignin related substances of the strain. The genomic analysis revealed the metabolic system of lignin related substances including guaiacylglycerol-β-guaiacyl ether (GGGE). In addition, we confirmed that GGGE metabolizing genes were arranged in a cluster in the genome of the strain. The homologs were detected from several microorganisms belonging diverse and phylogenetically distant clades within Sphingomonadaceae family. The transcriptome analysis revealed that expression of the genes related to assimilation of aromatic compounds and drug-resistance such as multi drug transporter increased when culturing this strain in the presence of GGGE**.**

Keywords: marine *Novosphingobiu,* genome and transcriptome analyses, guaiacylglycerol-β- guaiacyl ether, metabolic system

2015-P18

リグニンモデル 2 量体中 β-*O*-4 結合を開裂する海洋性 *Novosphingobium* 属細菌のゲノムおよびトランスクリプトーム解析

西　真郎、黒澤佳奈子、小林樹和、坪内泰志、秦田勇二、大田ゆかり

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Genome and transcriptome analyses of a marine *Novosphingobium* capable of cleaving the β-*O*-4 linkage in the lignin model dimer

Shinro Nishi, Kanako Kurosawa, Kiwa Kobayashi, Taishi Tsubouchi, Yuji Hatada, Yukari Ohta

Japan Agency for Marine-Earth Science and Technology (JAMSTEC), JAPAN

Abstract: We previously isolated a marine *Novosphingobium* from a sunken wood and detected β-*O*-4 cleavage activity of the isolate. In this study, we carried out genome and transcriptome analyses to understand the environmental response to lignin related substances of the strain. The genomic analysis revealed the metabolic system of lignin related substances including guaiacylglycerol-β-guaiacyl ether (GGGE). In addition, we confirmed that GGGE metabolizing genes were arranged in a cluster in the genome of the strain. The homologs were detected from several microorganisms belonging diverse and phylogenetically distant clades within Sphingomonadaceae family. The transcriptome analysis revealed that expression of the genes related to assimilation of aromatic compounds and drug-resistance such as multi drug transporter increased when culturing this strain in the presence of GGGE.

Keywords: marine *Novosphingobiu,* genome and transcriptome analyses, guaiacylglycerol-β- guaiacyl ether, metabolic system

2015-P19

Sphingobium sp. SYK-6 株におけるフェニルクマラン型化合物代謝に関与する 新規デカルボキシラーゼ遺伝子の解明

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Identification and characterization of novel decarboxylase genes involved in the catabolism of dehydrodiconiferyl alcohol in *Sphingobium* sp. strain SYK-6

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Abstract: *Sphingobium* sp. strain SYK-6 is able to utilize various lignin-derived biaryls including a phenylcoumaran-type compound, dehydrodiconiferyl alcohol (DCA). In the SYK-6 cells, the alcohol group of the B-ring side chain of DCA is initially oxidized to the carboxyl group to generate DCA-C. DCA-C is then converted to DCA-CC by the oxidations of the alcohol group of the A-ring side chain of DCA-C. DCA-CC is further degraded to 5-formylferulate and vanillin through the decarboxylation of the A-ring side chain and the following interphenyl cleavage between Cα and Cβ. In this study, we isolated and characterized decarboxylase genes for the conversion of DCA-CC. The *phcF*, *phcG*, and *phcH* genes, which conferred the DCA-CC decarboxylation activity on *Escherichia coli*, were isolated from the genomic library of SYK-6. These genes exhibited no significant similarity with known decarboxylases. Mutant analyses indicated that *phcF* and *phcG* have dominant roles for the conversion of DCA-CC. *phcF* and *phcG* were expressed in *E. coli*, and the resultant gene products were purified by Ni-affinity chromatography. Purified PhcF and PhcG catalyzed the decarboxylation of DCA-CC with activities of 70.9 U/mg and 36.7 U/mg, respectively. In addition, PhcF and PhcG appear to have different stereospcecificity toward DCA-CC enantiomers.

Keywords: dimer, biodegradation, bacteria, racemic, stilbene

2015-P20

Sphingobium sp. SYK-6 株のジアリールプロパン型リグニン由来化合物代謝 に関わる立体選択的変換酵素

小林将大1)、南保 美姫1)、上村 直史1)、菱山 正二郎2)、笠井 大輔1)、福田 雅夫1)、政井 英司1) 1)長岡技術科学大学・生物、2)森林総合研究所

Elucidation of the stereospecific catabolic pathway of a diarylpropane-type biaryl in *Sphingobium* sp. stain SYK-6

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Abstract: *Sphingobium* sp. strain SYK-6 is a degrader of lignin-derived biaryls, including β-aryl ether, diarylpropane, biphenyl, and phenylcoumaran. To date, a bacterial catabolic pathway of a diarylpropane-type compound, 1,2-bis(4-hydroxy-3-methoxyphenyl)-propane-1,3-diol (HMPPD), has been investigated only in *Pseudomonas paucimobilis* TMY1009. In this strain, HMPPD was subjected to Cγ-deformylation accompanied by dehydroxylation at the Cα position, resulting in the production of a stilbene-type compound. However, its reaction mechanism and the enzyme gene still remain unknown. In this study, we identified the HMPPD-converting enzyme genes of SYK-6 to fully characterize the catabolic pathway of HMPPD. In order to characterize the initial step of HMPPD degradation, the cofactor requirement in converting HMPPD was investigated. A conversion of HMPPD was observed only when NAD^+ was present, and the keto form of HMPPD (HMPPD-keto) was observed as the reaction product. Based on this result, we predicted the involvement of the Cα-dehydrogenase genes (*ligD*, *ligL*, and *ligN*), which are responsible for the catabolism of β-aryl ether, in the oxidation of HMPPD. The *ligD ligL ligN* triple mutant lost most of its ability to convert HMPPD, whereas this mutant was able to degrade HMPPD-keto. These results strongly suggest that HMPPD is catabolized via HMPPD-keto in SYK-6, and the Cα-dehydrogenase genes are indeed involved in this conversion. Enzyme analyses suggest that LigL and ligN converted the same stereoisomer of *threo*-HMPPD, while LigD converted the other stereoisomer.

Keywords: biodegradation, enantiomer, β-1 linkage, spirodienone, dimer

2015-P21

Sphingobium sp. SYK-6 株におけるβ-アリールエーテル代謝中間体の代謝経路及び酵素遺伝子の解明

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Investigation of the downstream pathway of the β-aryl ether catabolism in *Sphingobium* sp. strain SYK-6

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Abstract: In *Sphingobium* sp. SYK-6, a degrader of lignin-derived aromatic compounds, guaiacylglycerol-β-guaiacyl ether (GGE) is initially degraded to β-hydroxypropiovanillone (HPV) through the cleavage of the β-ether linkage. The resulting HPV is then oxidized to vanilloyl acetic acid (VAA) via vanilloyl acetaldehyde (VAL), and further catabolized through vanillate. In this study, we clarified the catabolic pathway of HPV and identified the genes involved in this pathway. The *hpvZ* gene, which conferred the HPV conversion activity on *Sphingomonas sanguinis* IAM12578 was isolated from the gene library of SYK-6. Mutant analyses and enzymatic characterization of the gene product demonstrated that *hpvZ* encodes a glucose-methanol-choline (GMC) oxidoreductase family protein essential for the conversion of HPV to VAL. In order to identify genes responsible for the conversion of VAL, putative 23 aldehyde dehydrogenase (ALDH) genes in SYK-6 were expressed in *E. coli*. The enzyme activity of these ALDH in the conversion of VAL was examined, and seven ALDHs demonstrated significant activity. Analyses of the conversion of VAA by cell extracts of SYK-6 in the presence of coenzymes suggest that VAA is degraded to vanillate through the formation of the coenzyme A ester of VAA.

Keywords: acetovanillone, Cγ oxidation, coenzyme A transferase, biodegradation, bacteria

2015-P22

バクテリアにおけるリグニン由来化合物の外膜輸送システム

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Bacterial outer membrane transport system for lignin-derived aromatic compounds

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Abstract: *Sphingobium* sp. strain SYK-6 is an alpha proteobacterium capable of utilizing various types of lignin-derived dimeric and monomeric compounds. To date, the catabolic enzyme genes for lignin-derived aromatics in SYK-6 have been extensively investigated. However, their uptake systems in bacteria are largely unknown. In this study, we focused on the uptake of lignin-derived aromatics across the outer membrane in SYK-6. DNA microarray analysis showed that the transcription of the *tbtA* gene proximal to the 5,5′-dehydrodivanillate (DDVA) catabolic gene cluster was specifically induced in the SYK-6 cells when grown in the presence of DDVA. Based on the amino acid sequence similarity, *tbtA* appears to encode a TonB-dependent receptor (TBDR). Disruption of *tbtA* in SYK-6 resulted in a growth deficiency on DDVA. Since outer-membrane localized TBDR is known to transport siderophore and vitamin B_{12} using proton motive force in consort with inner-membrane localized TonB-ExbB-ExbD complex, TBDR and the TonB complex appear to be involved in the outer-membrane transport of DDVA. In the SYK-6 genome, three *tonB* genes were found, and each of these genes was inactivated to examine their roles. As a result, the growth of a *tonB2* mutant on DDVA, vanillate, and syringate were significantly retarded. These results may suggest that the TonB complex-TBDR system is involved in the outer-membrane transport of lignin-derived aromatic compounds in SYK-6.

Keyword: Gram-negative bacteria, transporter, biphenyl, iron, proton motive-force

2015-P23

シロイヌナズナペルオキシダーゼ、AtPrx2, 25, 71 の発現解析による機能推定

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Expression analysis of lignification-related *Arabidopsis* peroxidase, *AtPrx2, 25, 71*

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Abstract: *Arabidopsis* peroxidase, AtPrx2, 25, 71, has been identified to be lignification-related plant peroxidase (Prx). The analysis measuring oxidative activity for guaiacyl type substrate, syringyl type substrate and polymer substrate showed that these three Prxs had different oxidizing property each other, and AtPrx71 had very similar oxidative property to CWPO-C. The property difference of lignin-polymerize-Prx may cause the inhomogeneity of lignin. In this study, we performed expression analysis using transformants introduced β-glucuronidase gene to investigate the functions of these Prxs, including lignification. The gene expression pattern varied by individual Prxs, and AtPrx71 expression pattern was similar to that of CWPO-C. These results suggest that three AtPrxs have different functions in lignification and/or differentiation, and AtPrx71 is the best functional homologue with CWPO-C among three AtPrxs.

Keywords: *Arabidopsis* peroxidase, oxidative property, lignification, promotor analysis, differentiation,

2015-P24

エタノール発酵性白色腐朽菌 *Phlebia* sp. MG-60 株のエタノール発酵メカニズムの解析

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Analysis of ethanol fermentation mechanism in ethanol fermentative white-rot fungus *Phlebia* sp. MG-60

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Abstract: White-rot fungus *Phlebia* sp. MG-60 shows higher ethanol production from several cellulosic materials containing lignin. In order to identify genes which are involved in ethanol production by *Phlebia* sp. MG-60, we analyzed the differential gene expression of *Phlebia* sp. MG-60 under the fermenting and non-fermenting conditions by next generation sequencing. As the results of the differential gene expression analysis, the genes which are involved in glucose uptake and metabolism, pyruvate metabolism, and ethanol synthesis were upregulated under the fermenting condition. To validate the reliability of expression profiles obtained using MiSeq, we selected four genes with higher expression levels under fermenting condition for real-time PCR (qRT-PCR) analysis. The results obtained from the qRT-PCR analysis were consistent with data from MiSeq.

Keywords: *Phlebia* sp. MG-60; ethanol fermentation mechanism; differential gene expression; Miseq

2015-P25

Preparation of dissolving pulp from sugarcane bagass by prehydrolysis and soda-AQ cooking method

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Abstract: Sugarcane (*Saccharum officinarum*) bagasse was used to produce dissolving pulp with combination of pre-hydrolysis followed by soda-anthraquinone (AQ) cooking and totally chlorine-free (TCF) bleaching. The TCF bleaching sequence composed of oxygen (O), peroxymonosulfuric acid (P_{sa}), and extraction with peroxide (E_p) stages. The addition of $MgSO_4$ was intended to maintain of pulp viscosities. Some results showed that the TCF sequence with Mg^{2+} addition obtained a higher viscosity than without Mg^{2+} application. However, Mg^{2+} had no positive effect on pulp brightness.

2015-P26

Properties of fibers prepared from oil palm empty fruit bunch for use as corrugating medium

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Abstract: This research was aimed at improving the utilization of waste generated by the palm oil industry by identifying the conditions needed to make fibers suitable for products such as paperboard from the empty fruit bunch (EFB) of oil palm (*Elaeis guineensis*). For this, the chemical pretreatment conditions needed to mechanically produce a pulp for paperboard were studied, as well as the effects of varying these conditions on the fiber properties. The optimum conditions to achieve the highest paper strength were found to be a NaOH dosage of 2 %, pretreatment time of 2 h at 121 ºC and refiner disk-clearance of 0.10 mm. The tensile index and tear index in this conditions are 19.7 kN.m/kg and 8.8 mN-m^2/g, respectively, similar with a pulp prepared from an old corrugated fiberboard box, and on the basis of this was considered acceptable for use in corrugating medium.

Keywords: oil palm empty fruit bunch, mechanical pulp, paperboard, fiber classification, tensile index

2015-P27

Structural alterations of lignin and carbohydrates of bamboo stems during prehydrolysis alkaline sulfite cooking

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Abstract: This study is aimed to investigate effects of prehydrolysis prior to alkaline sulfite cooking process on alterations of lignin and carbohydrate of bamboo (*Phyllostachys pubescens*). Prehydrolysis was performed at 150˚C for 1 to 3 h. The residue was then subjected to alkaline sulfite (AS)-anthraquinone (AQ) cooking with 30% active alkali (AA) dosage at 150˚C for 4 h. Syringil to guaiacyl ratio (S/V ratio) by CuO oxidation method of raw material was 1.9, with the total aldehydes yield 33.9%, and then its decreased to 0.35 after prehydrolysis for 3 hours and cooking. Prehydrolysis followed by AS-AQ cooking can enhance an increment of cellulose content, and decrements of hemicellulose, lignin and HexA contents. It is shown that lignin S/V ratio was decreased by prolonged prehydrolysis time.

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2016-101

大型イネ科バイオマス植物のリグノセルロース性状比較解析

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Comparative analysis of lignocellulose characteristics in large-sized gramineous plants

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Abstract: Large-sized gramineous plants are expected as potent biomass feedstocks for productions of biofuels and various biomass-derived materials especially because of their high biomass productivity. In this study, to gain insight into the relationship between cell wall structures and utilization characteristics of gramineous biomass, we comparatively characterized fractionated tissues of *Erianthus, Sorghum,* and sugarcane, in terms of their lignocellulose structures and enzymatic saccharification efficiency. 2D NMR and a series of cell-wall chemical analyses revealed tissues specific assembly of wall polysaccharides and different types of lignin polymers. Enzymatic saccharification efficiency was negatively correlated with lignin content for *Sorghum* and sugarcane tissues but not for the tissues from *Erianthus*. Our data suggest that lignin content is not the only factor affecting the enzymatic saccharification efficiency of gramineous biomass.

Keywords: lignification, monocot, bioethanol, biorefinery, bioresource,

2016-102

選択的^{13}C標識法と固体NMR測定によるリグニンの構造解析

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Structural analysis of lignin by a selective ^{13}C labeling technique combined with solid-state ^{13}C NMR

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Abstract: Lignin is one of the main components of wood cell walls, which has a highly complicated structure biosynthesized by radical coupling of monolignols. To elucidate the lignin structure, selective ^{13}C-enriched lignin was produced by an administration of the selective ^{13}C-labeled precursor to wood and analyzed by solid-state ^{13}C-NMR. In this study, we synthesized [ring 5-^{13}C] coniferin and fed to *Ginkgo biloba*. The lignin was obtained by a ball milling followed by enzyme treatment. From the difference NMR spectrum made by subtraction of the spectrum of the un-enriched enzyme lignin from that of the ^{13}C-enriched enzyme lignin, quantitative determination was made on the frequencies of major inter-unit bonds. From the result, the frequency of the uncondensed structure was about 30%, which was lower than the previously reported values. It should be owing to the cleavage of β-O-4 bond during the ball milling.

Keywords: solid-state ^{13}C-NMR, ^{13}C-labeled coniferin, thioacidolysis, quantitative determination, uncondensed structure, ball milling

2016-103

β–1 型構造に関する研究：3 量体モデル化合物の NMR データに基づく広葉樹リグニン中のスピロジエノン構造の同定

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Study on β–1 structures in lignin: Identification of spirodienone structure in hardwood lignin based on the NMR data of its trimeric model compound

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Abstract: A trimeric lignin model compound for spirodienone structures (β–1/α–O–α′) was prepared by oxidative coupling of sinapyl alcohol γ-acetate with a phenolic β–O–4 dimer model. The ^{1}H and ^{13}C NMR chemical shifts of the spirodienone compound were compared in an acetate form with the candidate signals for spirodienone structures observed on the HSQC spectrum of acetylated hardwood lignin (MWL). The chemical shifts of the signals from the lignin were in good agreement with those of the model at α, β, and γ-positions in one side-chain part, α′ and β′-positions in another side-chain part, and 2′ and 6′-positions in the dienone moiety.

Keywords: milled wood lignin, guaiacyl-syringyl, avicennia, diarylpropane, radical coupling

2016-104

モノリグノール配糖体の脱水素重合によるフェニルグリコシド型LCC形成の可能性

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Possibility of phenyglycoside-type LCC formation by dehydrogenative polymerization using monolignol glycoside

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Abstract: HRP-catalyzed dehydrogenative polymerization of coniferyl alcohol in the presence of coniferin afforded the corresponding dehydrogenation polymer (CG-DHP-1) in 104 % yield. HSQC-NMR spectrum of CG-DHP-1 showed that coniferin was non-enzymatically incorporated into lignins via nucleophilic addition to quinomethide intermediates. On the other hand, HRP/ β-glucosidase-catalyzed dehydrogenative polymerization of coniferin afforded the corresponding dehydrogenation polymer (CG-DHP-2) in 84 % yield. HSQC-NMR spectrum of CG-DHP-2 showed not only that coniferin was directly incorporated into lignins, but also that coniferin was incorporated into lignins via isoconiferin which is produced from coniferin by transglycosylation.

Keywords: coniferin, isoconiferin, lignin carbohydrate complex, phenyl glycoside, syringin

2016-105

マイクロダイセクション:
ポプラ1年輪内のリグニン単位間結合変化の解析

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Microdissection : The analysis of lignin internal linkage changing in the growth ring of *Populus alba*

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Abstract: Lignification is known to occur in xylem tissue before programmed cell death (PCD). Recently, it is suggested that lignification still proceeds after PCD in some reports, and our previous study also indicated the similar results; the yields of pyrolysis products and S/G ratio, which derived from β-O-4 linked lignin determined by laser micro dissection (LMD) and pyrolysis-GC-MS (Py-GC-MS), increased and decreased, respectively, along with the radial direction within a growth ring in which the xylem fiber cells were already suffered from PCD. In order to understand more detailed lignification process, in this study we analyzed β-β, β-1, β-5 internal linkage in lignin using LMD and Py-GC-MS. First, we examined detection limit of Py-GC-MS for these dimeric pyrolysis products from the dissected samples prepared by LMD. The minimum requirement of the dissected area was 0.3 mm^{2} in. Then, the abundances of β-β, β-1, β-5 subunits in wood meal prepared from old poplar stem, lignified fiber cells and unlignified fiber cells in a year-old *P. alba* stem were compared. β-1 subunit was found in a young stem but not in wood meal, which indicate that β-1 is formed at an early stage in differentiation of xylem fiber cells.

Keywords: laser micro dissection, Py-GC-MS, lignin dimer, xylem, fiber

2016-106

シロイヌナズナ植物体および培養細胞を用いたリグニンモノマー輸送候補　遺伝子の発現解析

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Expression analysis of lignin monomer transporter candidate genes in Arabidopsis plant and cell culture

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Abstract: Monolignol transport from the cytosol to the cell wall is essential step for lignification because monolignols are synthesized in the cytosol and polymerized in the apoplast. Previously, some studies suggested that ATP-binding cassette (ABC) transporters have potential to transport monolignol across the plasma membrane in *Arabidopsis thaliana*, thus screening of monolignol transporter among ABC transporters were attempted in this study. In the first screening, ten ABC transporters that are conserved in only vascular plant, *A. thaliana* but not in non-vascular plant, *Physcomitrella patens* were selected. Parallel screening was made by the monitoring of the gene expression with real-time PCR using tracheary element induction system of the *A. thaliana* cell culture. The expression profile of selected candidate transporter genes in each plant organ was analyzed with real-time PCR using *A. thaliana* intact plants. Positive correlation between monolignol synthesis genes and the five selected transporter genes suggested that these transporters may be related to lignin biosynthesis.

Keywords: *Arabidopsis thaliana*, monolignol, extracellular transport, ATP-binding cassette transporter, real-time PCR

2016-107

改変型植物酸性 peroxidase の酵母での発現と精製(5)

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Heterogeneous expression and purification of modified plant peroxidase (5)

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Abstract: Most of plant peroxidases can oxidize coniferyl alcohol efficiently, but not sinapyl alcohol. On the other hand, a few of plant peroxidases were reported to use sinapyl alcohol as preferred substrates. They were guessed to have the additional active sites in the other positions than the heme pocket in the active site. We tried to introduce the additional catalytic sites of these peroxidases to PrxA3a, an anionic peroxidase of hybrid aspen, *Populus* X *kitakamiensis*, for substrate specificity modifications and for certifications of the surface amino acid residue hypothesis. As a result, PrxA3a A165W and PrxA3a F77Y, PrxA3a F77Y A165W raised the oxidizing activity of cytochrome *c* which cannot enter into the heme pocket. Furthermore, PrxA3a F77Y, PrxA3a F77Y A165W, and PrxA3a F77Y L182Y gained sinapyl alcohol polymerizing activity. We analyzed shifts of Soret band absorption by H_2O_2 treatment. The responses to the H_2O_2 of Soret band absorption differed in mutated PrxA3a enzymes and wild type. Therefore, it is thought that electron transfer is occurred between heme and mutated amino acid residues. The gel filtration analysis showed that PrxA3a AW and PrxA3a FYAW could polymerize sinapyl alcohol efficiently.

Keyword: lignin, PrxA3a, soret band, HPLC, sinapyl alcohol

2016-108

リグニン・多糖複合体分解酵素の植物体での発現(2)

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Expression of a lignin-carbohydrate complex degrading enzyme in plants (2)

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United Graduate School of Agricultural Science, Tokyo University of Agriculture and Technology

Abstract: We aim to increase the industrial values of crops by improvement of the digestibility of the forage crop and conversion rate to saccharification from biomass. We have been challenging to modify the lignin content and structures, by suppression of the genes for the lignin biosynthetic pathway or expression of lignin degradation enzymes. In this research, we tried to reduce the linkages between lignin and carbohydrate by introduction of a lignin-carbohydrate-complex decomposition enzyme gene to rice plants. CcEST1 is an esterase and CcAbf62A is an arabinofuranosidase of a white-rot-fungus, *Coprinopsis cinerea*. These enzymes can cut bonds between the lignin and polysaccharide. CcEST1 has feruloylesterase and acetyltransesterase activities.

CcAbf62A has activity for arabinoxylan, one of hemicelluroses. We altered the genes to effectively secrete to the plant extracellular space and induced to rice plants. We checked introduction of each gene by PCR. There were no seriously changes in the phenotypes of CcEST1 introduced rice plants. But, one CcAbf62A introduced rice plant represented dwarf and abnormal tillering phenotypes.

Keywords: lignin, *Oryza sativa*, *Coprinopsis cinerea*, esterase, arabinofuranosidase, *Agrobacterium tumefaciens*, degrading enzyme, lignocarbohydrate complex, *prxA3a*

2016-109

リグニン含量が極端に異なるハイブリッドユーカリ系統の遺伝子発現解析

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Transcriptome Analysis of Hybrid Eucalyptus with Contrasting Lignin Content

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Abstract: *Eucalyptus* is one of the most important commercial temperate hardwoods for the pulp and paper industries because of its fast growth and good pulp production characteristics. In this study, we compared transcript levels involved in secondary cell wall synthesis related genes to find out DNA markers. First, we measured Klason lignin content of 918 hybrid Eucalyptus *(Eucalyptus urophylla* x *E. grandis*) trees by Near-Infrared spectra. These trees were composed of 20.2–35.5% of Klason lignin content with normal distribution. Among them, we selected two genotypes that have contrast lignin content for further analysis. AM063 and AM380 had 20.2 and 35.5% of Klason lignin content, respectively. The correlation between wood properties and transcript levels of wood formation-related genes was investigated by RNA-seq. No significant differences of transcript levels of ten cellulose synthase and four sucrose synthase genes were observed in both genotypes. AM063 exhibited higher transcript levels of UDP-glucose pyrophosphorylase and xyloglucan endotransglucosylase than those in AM380. Most monolignol biosynthesis-related isozyme genes showed significantly higher transcript levels in AM380. Higher transcript levels of the genes encoding NAC, WRKY, AP2/ERF, and HD transcription factors in AM380 were observed. We also found increased transcription of several MYB and LIM domain transcription factors in AM380 as compared to AM063. These results show that genes related to monolignol biosynthesis may regulate the wood composition.

Keywords: hybrid Eucalyptus, lignin, cellulose, hemicellulose, RNA-seq

2016-110

二次細胞壁形成で発現する遺伝子の網羅的機能解析と木質バイオマス改変技術の開発

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A comprehensive functional analysis of secondary cell wall formation-associated genes and its application for genetic engineering of woody biomass utilization

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Abstract: This study aims (1) to identify more key players regulating secondary cell wall (SCW) formation, and (2) to develop genetic tools for engineering SCWs. We have prepared hundreds of *Arabidopsis* homozygous lines expressing more than 50 genes of our interest at the very early stage of SCW formation. While most lines grew like wild-type, their woody tissue samples showed different levels of susceptibility to an enzymatic degradation under a very mild pretreatment condition. Some lines showing the high enzymatic digestibility had modified xylan or lignin.

Keywords: 101 genes project, xylem-specific overexpression screen, hot compressed water pretreatment

2016-111

ヘミセルロースの合成阻害による細胞壁成分への影響

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The effect of the inhibition of hemicellulose synthesis on cell wall composition

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Abstract: To elucidate the role of hemicellulose in plant cell wall, its synthesis was inhibited by RNAi method. In our study, target gene is UDP-glucuronic acid decarboxylase (UDP-xylose synthase, UXS) which converts UDP-xylose from UDP-glucuronic acid. In rice (*Oryza sativa*), the genes for UXS are consisted as a multi gene family with five clones. During elongation period of rice, the expression level of *UXS3* was the most abundant among UXS gene family. To suppress this gene, *UXS3*-RNAi vector was constructed and introduced into rice. Almost transgenic rice (*UXS3*-RNAi) strains were dwarfing compared to wild type, and they showed sterility. The expression of *UXS3* in transgenic rice was inhibited. Interestingly, *PAL* and *4CL* involved in lignin biosynthesis were also inhibited in proportion to the *UXS3* expression level. The composition of cell wall was analyzed to show the decrease of xylose and therefore hemicellulose, in contrast cellulose content was increased. As expected in the expression of lignin biosynthesis genes, the lignin content was also reduced. This was derived from decrease of xylose, arabinose and ferulic acid binding to lignin. Therefore, it showed the possibility to regulate lignin biosynthesis by *UXS3* regulation.

Keywords: rice, UDP-glucuronic acid decarboxylase, PAL, 4CL, cellulose

2016-112

順遺伝学アプローチを起点とした、リグニン分解酵素活性およびリグニン生分解に重要な新たな因子の探索

中沢威人 1)、小寺里奈 1)、西村裕志 2)、坂本正弘 1)、渡辺隆司 2)、本田与一 1)
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Forward genetics study in the white-rot agaricomycete *Pleurotus ostreatus* suggested unidentified factors are important in the ligninolytic system

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Abstract: White-rot fungi play an important role in global carbon cycle because they are the only known organism that biodegrade wood lignin. Lignin peroxydases (LiPs), manganese peroxidases (MnPs) and versatile peroxidases (VPs) are considered to be key players in the ligninolytic system. However, there may remain unidentified factor(s) important in the ligninolytic system. Classical genetics or forward genetics, isolation of mutants followed by identification of the gene responsible for a mutant phenotype, is a straightforward strategy to identify such factor(s). We successfully identified three genes important in decolorization of dyes, model compounds to examine the ligninolytic activity in the white-rot fungus *Pleurotus ostreatus*. Examination of the effects of the mutations on gene expression, enzyme activity and wood lignin biodegradation suggested a complicated mechanisms underlying the ligninolytic system.

Keywords: white rot, fungal genetics, peroxisome, RNA-seq, transcriptional regulation

2016-201

リグノセルロースバイオリファイナリーのためのリグニン・ペプチド間相互作用解析

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Analysis of interaction between lignin and peptides for lignocellulosic biorefinery

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Abstract: Highly selective degradation of lignin is pivotal for lignocellulosic biorefinery. However, few studies have examined natural and synthetic molecular components recognizing the heterogeneous aromatic

polymer. We identified lignin-binding 12-mer peptides using a phage display technique. The selected peptides were found to possess a characteristic sequence and exhibit structure-dependent high-affinity binding to the lignin isolated from softwood and hardwood. To characterize the key amino acid residues in the lignin-binding peptides, a peptide designated as C416 and its single-residue substituted peptides were subjected to the binding analysis with MWL from softwood and hardwood.

Keywords: peptide, lignin, phage display, SPR, MWL

2016-202

高活性リグニン分解菌 *Phanerochaete sordida* YK-624 株によるネオニコチノイド系殺虫剤の分解及び無毒化

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Degradation and detoxification of the neonicotinoid insecticides by the white-rot fungus *Phanerochaete sordida* YK-624

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Abstract: Clothianidin (CLO) and nitenpyram (NIT) are the family of the neonicotinoid pesticides, which have been widely used over the last two decades. However, its toxicity for insects and neurological toxicity for humans are serious problems. Here, the degradations of CLO and NIT by the white-rot fungus *Phanerochaete sordida* YK-624 were examined in nitrogen-limited liquid medium. After incubation for 20 days at 30 °C, 37% of CLO was degraded in the cultures. In contrast, after incubation for 5 days at 30 °C, 100% of NIT was degraded in the same cultures. High-resolution ESI-MS and NMR analyses of the culture supernatant metabolite identified *N*-(2-chlorothiazol- 5-yl-methyl) -*N'*-methylurea (TZMU) as a metabolite of CLO degradation. Similarly, We identified (E)-*N*-((6-chloropyridin-3yl) methyl)-*N*-ethyl-*N'*-hydroxyacetimidamide (CPMHA) as a metabolite of NIT degradation. The addition of cytochrome P450 inhibitors to the culture medium caused the reduction of CLO degradation by *P. sordida* YK-624. The viability of the neuronal cell line Neuro2a by the effects of CLO and TZMU demonstrated that *P. sordida* YK-624 effectively degrades CLO into a metabolite that lacks neurotoxicity.

Keyword: *Phanerochaete sordida* YK-624; clothianidin; nitenpyram; bioremediation

2016-203

ブナ木粉中リグニンの酵素的分解反応最適化の試み

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Optimization of enzymatic lignin degradation in beech woods by manganese peroxidase

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Abstract: Woody biomass is the most abundant biomass, and it is expected the utilization as biorefinery feedstock. However, lignin which is a recalcitrant aromatic polymer contained in wood, and prevents the breakdown of cellulose and hemicellulose. In this study, we attempt to optimize the enzymatic system that degrades lignin in beech wood by manganese peroxidase (MnP) from *Phanerochaete sordida* YK-624. At first, we investigated the effect of the combination of the radical mediators in the enzymatic delignification reaction. Although some of combinations have not improved the lignin degradation, many of radical mediator combination have been improved lignin degradation. In addition, lignin degradation rate was further improved by the addition of cellulases. Therefore, it is suggested that the simultaneous saccharification and delignification reaction is much effective for the enzymatic delignification.

Keywords: *Phanerochaete sordida* YK-624, manganese peroxidase, lignin degradation, radical mediator, saccharification

2016-204

ルテニウム錯体結合型アミノ酸触媒を用いるリグニンおよびモデル化合物の酸化的分解

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Ruthenium complex-bound amino acid-catalyzed oxidative degradation of lignin and model compounds

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Abstract: An efficient oxidative degradation of lignin into useful aromatic compounds has been developed by using H_2O_2 as a terminal oxidant and in the presence of a catalytic amount of ruthenium complex-bound amino acid **1**. Model compounds of the lignin substructures, such as benzyl alcohols, methoxybenzenes, and β-O-4 dimer models can be oxidized under the degradation conditions to give the corresponding 1,4-benzoquinones, phenols, aromatic aldehydes, and aromatic ketones. The oxidative degradation of milled wood lignin (MWL) and wood powder obtained from Japanese cedar gives 2-methoxy-1,4-benzoquinone selectively, demonstrating the efficiency of ruthenium complex-bound amino acid catalyst **1**.

Keywords: Ruthenium catalysis, Metalated amino acid, Oxidation, Aromatic biorefinery, 2D NMR

2016-205

フェノール性水酸基をメチル化した木粉の
マイクロ波ソルボリシスにより得られるリグニンオリゴマーの構造解析

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Structural analysis of lignin oligomers released by microwave solvolysis of wood obtained after methylation of free phenolic hydroxyl groups

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Abstract: An acid-catalyzed toluene-methanol solvolysis method can release lignin oligomers from wood. In this study, phenolic end groups in lignin were selectively methylated to investigate how the phenolic units influence on release of lignin oligomers during solvolysis. Thioacidolysis analysis of TMS-CH_2N_2 methylated wood sample showed that about 17% of guaiacyl units corresponded to terminal units with free phenolic groups. Thioacidlysis and subsequent Raney nickel desulfuration showed that lignin dimeric compounds derived from terminal units with free phenolic groups were detected only for β-1 and β-5 linkages, not for 5-5, β-β, and 4-*O*-5 bonds. In particular, the relative abundances of the β-*O*-4-linked β-1 dimers derived from phenolic terminal units were significantly higher than those of β-5 linkages. This result may relate the fact that the β-1 dimers are more easily detected during solvolysis compared to the other linkage types.

Keywords: lignin, interunit linkages, thioacidolysis, trimethylsilyl diazomethane, solvolysis.

2016-206

リグニン結合性有機物担持前加水分解による天然リグニンの構造制御

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Structural control of native lignin during prehydrolysis by sorption of a lignin-binding organic compound

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Abstract: Prehydrolysis using dilute acid was conducted for wood meal sorped with *p*-cresol. The residue was treated in sodium hydroxide solution at 170 ºC. After acidification of black liquor, dioxane-soluble and ether-insoluble lignin was recovered. FT-IR spectrum of the lignin indicated that *p*-cresol was grafted to native lignin during dilute acid prehydrolysis. An aromatic dimer with phenyl coumaran-type structure was also recovered, indicating that cleavage of β-O-4 linkages occurred in alkaline condition by nucleophilic attack of *p*-cresol grafted to α-carbon of native lignin. The sorption of *p*-cresol could be an effective method to control the lignin structure during prehydrolysis.

Keywords: dilute acid, prehydrolysis, wood, *p*-cresol, functional lignin

2016-207

第四級アンモニウム塩を反応媒体としたリグニンの高選択的分解

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Selective conversion of lignin with quaternary ammonium salts as a reaction medium

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Abstract: Lignins such as milled wood lignin, sodium lignosulfonate, and soda lignin and Japanese cedar (*Cryptomeria japonica*) wood flour, were degraded in tetrabutylammonium hydroxide 30-hydrate, NBu4OH·30H2O, at 120 ºC. The degradation for 72 h gave vanillin with surprisingly high yields, e.g. the milled wood lignin gave vanillin with 11.5 wt%. Degradation in an aqueous NaOH solution with the same OH^- concentration resulted in much less vanillin yield, which strongly suggests that the NBu_4^+ cation was responsible for the high yield of vanillin. Discussion on the mechanisms in the effects of the NBu_4^+ cation was made on the basis of further model experiments and pulping mechanisms reported previously.

Keywords: degradation, quaternary ammonium, vanillin, alkali

2016-208

Stereo-preferential degradation of the *erythro* and *threo* isomers of *β*-O-4 type lignin model compounds under hydrogen peroxide bleaching conditions and its relation to the type of major degradation products

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Abstract: The *erythro* (***E***) or *threo* (***T***) isomer of a dimeric non-phenolic *β-O*-4-type lignin model compound, 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (***E*** isomer or ***T*** isomer, respectively), was individually reacted with hydroxyl and/or oxyl anion radicals generated by the decomposition of hydrogen peroxide under a condition similar to hydrogen peroxide bleaching to observe the stereo-preference of these radicals toward the ***E*** or ***T*** isomer. The stereo-preference of oxyl anion radical was intrinsically the ***E*** isomer, but conversely the ***T*** isomer in the reaction at a high pH where the *α*-hydroxy group of the ***E*** isomer was hypothesized to dissociate. This dissociation generates the electrostatic repulsion between negatively charged oxyl anion radical and the side-chain of the ***E*** isomer. Hydroxyl radical had almost no stereo-preference, probably owing to its high reactivity to the aromatic nucleus. As the major degradation products, veratraldehyde and veratric acid were obtained with relatively high yields at high pH levels.

Keywords: delignification, diastereomer, pulp, bleaching, alkyl-aryl ether

2016-209

熱分解温度を考慮したグアイアコールからのコーク、多環式芳香族化合物及びその他芳香族化合物の生成機構

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Temperature-dependent conversion mechanisms of guaiacol into coke, polycyclic aromatic hydrocarbons, and other aromatic compounds

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Abstract: Guaiacol and its alkyl-substituted derivatives are the important intermediates during lignin pyrolysis, which degraded further into coke (solid carbonized products), polycyclic aromatic hydrocarbons (PAHs) and other aromatic compounds including cresols, catechols, benzene and toluene along with the noncondensable gases. In this paper, formation and degradation behaviors of 23 compounds during pyrolysis of guaiacol were investigated under nitrogen in the temperature range 300-600 ºC. Some compounds were pyrolyzed independently to understand their roles in the product formation. Based on these results, lignin conversion mechanisms during pyrolysis are discussed in terms of the temperature effects. These results would provide insights into the useful bio-chemicals production from lignin and mitigation of tar trouble in wood gasification.

Keywords: lignin, pyrolysis, polycyclic aromatic hydrocarbon, methoxyl group, mechanism

2016 特別講演

超・亜臨界流体技術によるリグノセルロースのトポ化学

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Invited lecture: Topochemistry of lignocellulosics by supercritical/subcritical/fluid technologies

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Abstract: Global warming and depletion of fossil fuels are recently causing many problems. Under such a situation, a special attention has been paid to lignocellulosics for useful energy and chemicals. Therefore, in this study, evolution and biodiversity of various biomass species were first introduced so as to discuss topochemistry of lignocellulosics. In addition, the behaviors of lignocellulosic decomposition were evaluated for biobased energy and chemicals as treated by supercritical/subcritical fluid technologies, focusing on topochemistry of lignin.

Keywords: chemical composition, biosynthesis, wood cell wall, softwood, hardwood, solvolysis

2016-210

木材の熱安定性に及ぼすリグニンの影響

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Influence of lignin on wood thermal stability

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Abstract: Heterogeneous layered structure of wood cell wall, which consists of assembling cellulose microfibrils covered by the hemicellulose-lignin matrix, is expected to influence the thermal stability of wood consisting polymers. In this study, thermal stabilities of Japanese beech (a hardwood) and Japanese cedar (a softwood) were compared with those of their holocellulose, milled wood lignin (MWL) and hemicellulose fractions by using thermogravimetry (TG) (N_2/ 10 °C/min). As a result, the derivative of TG (DTG) peaks and shoulders of wood samples were shifted to the lower temperature regions for holocelluloses, where the peak and shoulder temperatures were rather close to those of cellulose (Avicel PH-101) and the isolated hemicelluloses, respectively. Thus, lignin would stabilize hemicellulose and cellulose in wood cell wall against thermal degradation. Interestingly, DTG shoulder temperatures of wood and demineralized wood samples were very close to those of MWL + 2%KOAc (a model of metal uronate in xylan) and MWL, respectively. These results lead to an interesting hypothesis: hemicellulose in wood cell wall becomes reactive when lignin thermal degradation (depolymerization) occurs, since hemicellulose is stabilized by covering with lignin polymers.

Keywords: pyrolysis, thermal stability, hardwood, softwood, stabilization effect of lignin

2016-211

リグニンアナログの溶液中における構造

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Structure of lignin analogues in solution

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Abstract: Size exclusion chromatography with a detector of multi-angle laser light scattering was attempted for lignin analogues, polymeric lignin model exclusively comprised of β-*O*-4’ linkages and amphipathic lignin derivatives to investigate their structures in solution. The lignin model compound exhibited a similar swelling behavior in chloroform to that of polystyrene. The lignin derivatives formed self-aggregates in chloroform, and the aggregates had more compact structure than polystyrene with the same molecular mass.

Keywords: SEC-MALS, lignin structure, Mark-Houwink-Sakurada equation, light scattering

2016-212

木材の物性研究からみえるリグニン

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Lignin from the view of wood physics researches

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Abstract: We have obtained many interesting results about lignin by various measurements of physical properties such as viscoelastic properties, thermal characteristics, and adsorption characteristics. And, it was considered how molecular state of lignin was present in cell wall or what kinds of role was played by lignin in wood based on these results. The followings are some of the information. Thermal softening temperatures and apparent activation energy of lignin in water-swollen wood were different among Japanese hardwood, tropical hardwood and coniferous wood, and these were decreased with decrease in the amount of lignin or crosslinking density, and these were also changed by drying history or cooling speed after heating. In addition, the value of micro pores with a pore size of several Å based on lignin was decreased and the specific heat was changed significantly by heat treatment. In this debating society, these information would be explained together, and presence state and role of lignin in wood be comprehensively discussed.

Keywords: wood physics, viscoelastic property, thermal characteristics, adsorption characteristics, crosslinking density

2016-213

リグニンを原料とするタンデム型電気２重層キャパシタ用電極の開発

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Development of electrodes for internal tandem electric double layer capacitors (IT-EDLCs) derived from lignin

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Abstract: To fabricate electric double layer capacitors (EDLCs) with a wide potential window and a high energy density in an EDLC package, electrodes derived from lignin based activated carbon fibers (ACFs) were internally laminated and connected in series, in parallel, or in a series/parallel combination, which are named as internal tandem (IT) EDLCs in this article. As expected, the potential window was expanded by the series connection, and the capacitance was increased by the parallel connection. The energy density in the parallel-connected EDLC was remarkably increased by 66% (16.6 Wh kg^{-1}) compared with that of a single cell type EDLC. The EDLC with the combination connection showed both advantages.

Keywords: electric double layer capacitor (EDLC), energy density, power density, functionalization, value-added material

2016-214

PEG・バイサルファイト法によるタケリグニン液化物から調製したポリウレタンフォームの特性評価

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Characterisation of polyurethane foam prepared from liquefied bamboo-lignin by PEG-bisulfite method

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Abstract: Liquefaction of bamboo was performed by polyethylene glycol (PEG)-bisulfite method. A retention rate of lignin in liquefied bamboo was depended on treatment temperature and reaction times. Additionally, polyurethane foam, prepared from the liquefied bamboo, was showed high storage elastic modulus than control sample of PEG using solid viscoelasticity measurement. This PEG-bisulfite liquefaction can be one of plausible method for the biorefinery of bamboo and bamboo lignin.

Keyword: lignin, bamboo biorefinery, polyurethane foam, PEG-bisulfite method, viscous elasticity

2016-P01

広葉樹の葉リグニンの DFRC 法による検出（3）

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Detection of broad-leaf lignin in angiosperms by DFRC analysis (3)

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Abstract: The DFRC (**D**erivatization **F**ollowed by **R**eductive **C**leavage) analysis can be used to detect lignin specifically from tree leaves, since it gives C6-C3 type degradation products by the cleavage of arylether linkages of lignin, excluding other (poly)phenolic substances. In this study, the distribution of lignin in beech leaf was investigated in detail to find out the heterogeneity in lignin composition. Leaf vein separated from beech leaf contained lignin with low S/G ratio, and other blade tissue had apparently syringyl-rich lignin. The hypothesis that these syringyl lignin in leaf tissue has some defensive roles against light stress was denied by the results of increased S-lignin in leaves under weaker light condition.

Keywords: leaf lignin, DFRC method, vein, stress defense

2016-P02

Tetra-*n*-butylphosphonium hydroxide を用いた新規リグニン定量法の開発

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A novel lignin quantitative analysis using tetra-*n*-butylphosphonium hydroxide

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Abstract: Tetra-*n*-butylphosphonium hydroxide (TBPH, [P$_{4,4,4,4}$]OH) is a kind of ionic liquids, and known to have the whole wood dissolution ability. In this study, TBPH was introduced to determine lignin content in cedar wood. An analytical procedure of the TBPH method was developed, and its practical reliability was investigated. A series of compression cedar wood meal and 60% TBPH aqueous with peroxide were mixed in a glass tube and treated in an autoclave for 3 h at 121 ºC. After the treatment, solution was diluted with alkaline water-methanol mixture, and precipitation of carbohydrates was removed by centrifugation. 280nm UV absorptions of the TBPH solution was measured, and lignin contents were calculated with the lignin coefficient 26.7 l g^{-1} cm^{-1}. Lignin contents determined by the TBPH method showed good correlation (R^2=0.78) with those by the Klason method. This correlation factor was nearly the same level as that of the acetyl bromide method (R^2=0.71). In total, the TBPH method could be a novel lignin quantitative analysis with good reliability, safety, and time & labor efficiency.

Keywords: ionic liquid, TBPH method, Klason method, acetyl bromide method, multi-sample analysis

2016-P03

天然リグニン中の β—β（レジノール）構造の結合様式

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The bonding sites to β-β substructure in natural lignin

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Abstract: A β-β substructure accounts for about 10 % of lignin. In biosynthesis, the β-β substructure is formed only from the coupling of monolignols at the β-position, then in this case, lignin polymerization from this structure continue to two directions by further couplings. Then, in our previous research, it was reported that the β-β substructure played an important role in the bonding sites between lignin and xylan. It is considered that the information about the β-β substructure in lignin molecules is important for the elucidation of lignin chemical structures such as LCC. In this study, the natural lignin was degraded and the obtained degradation products were analyzed by LC-MS for considering whether the β-β substructure is in the molecule or at end of the molecule. In the degradation of lignin, the β-β substructure remained because β-O-4 linkages in MWL were selectively cleaved by the γ-TTSA method. When the degradation products were monitored with mass chromatograms for m/z 419 and m/z 573, syringaresinol and syringaresinol monotosylate,derived from the β-β substructure in MWL, were found. This result shows that the β-β substructure in natural lignin exists not only in the molecule but also at the end of the molecule.

Keywords: β-β substructure, LC-MS, MWL, syringaresinol

2016-P04

トウモロコシ穂軸の各形態部位の構造解析

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Structural analyses of three morphological regions of corn (*Zea mays*) cob

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Abstract: Corn (*Zea mays*) cob is composed of three morphological regions: chaff, woody ring and pith. In this study, the cell wall components in these morphological regions were characterized. It was found that the chemical compositions in three regions were relatively similar, and that hemicellulose was the main component and the lignin contents were in a range between 15 and 20%. Through the alkaline nitrobenzene oxidation analysis, lignin in all regions was composed of guaiacyl, syringyl and *p*-hydroxyphenyl lignins, while their ratios were different. Furthermore, the amounts of ferulic acid and *p*-coumaric acid, which associate with corn lignin, are different between three regions. Accordingly, it seems that there are some differences in the lignin structure among three morphological regions.

Keywords: cinnamic acids; corn cob; hemicellulose; alkaline nitrobenzene oxidation; morphological regions

2016-P05

高等植物の光屈性反応における光照射側組織での成長抑制メカニズム

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Regulation of phototropic response in the early stage by blue light-mediated growth inhibitors

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Abstract: The growing shoot of plant seedlings always *bend* towards the *light source*. This *phenomenon* is known as *phototropism*. This mechanism has been believed as the result of light-mediated lateral *redistribution of auxin (Cholodny-Went theory).* On the other hand, the second model which is generated by light-mediated growth inhibition has also been proposed in the early stage of phototropism (Bruinsma-Hasegawa theory). In this research, we examined the inhibitory mechanism of shoot growth regulated by light-induced growth inhibitors in pea and maize seedlings. The activity of inhibitors against the auxin-induced shoot elongation and the induction of cell-wall stiffness will be discussed.

Keywords: auxin antagonist; cell-wall stiffness; lignin accumulation; maize, pea; phototropism

2016-P06

二次壁肥厚を促進するイネ転写因子 OsSWN1 を過剰発現するシロイヌナズナ *cad-c/cad-d* 二重変異体の解析

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Analysis of *Arabidopsis cad-c / cad-d* double mutant overexpressing the rice transcription factor OsSWN1 that enhances secondary cell wall thickening

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Abstract: Second-generation biofuels and biomaterials produced from non-food lignocellulose biomass are seen as a good prospect, and rapidly increasing concern due to the depletion of petroleum resources and related environmental issues. Typically, most of the lignocellulosic biomass is comprised of cellulose, hemicellulose and lignin. Cellulose and hemicellulose are major structural components of plant cell wall and assumed to be converted for biofuels and biomaterials. Whereas, lignin is complex polymer and cross-links with cellulose and hemicellulose. Effectively removal of lignin is considered as the crucial step for preparing of cellulosic ethanol from lignocellulosic biomass. *N*AC *S*econdary wall *T*hickening factors (NST) can effectively enhance the secondary cell wall formation. Previous study inferred that except for the vascular vessels, the secondary wall thickenings are quelled by knockout of the two genes *NST1* and *NST3* in Arabidopsis [1]. *OsSWN1* in rice is the orthologue of the *NSTs* in Arabidopsis. Overexpression of *OsSWN1* in *nst1 nst3* double mutant of Arabidopsis driven by the *NST3* promoter showed that, secondary wall thickenings are observed in pith cells and also in interfascicular fibers of inflorescence stems [2]. When *OsSWN1* gene overexpressing in poplar plants, secondary wall thickenings are significantly facilitated compared to wild type plants [3]. In this study, for further application, we analyzed the Arabidopsis *cad-c / cad-d* double mutant overexpressing *OsSWN1*.

Keywords: *Arabidopsis thaliana*; secondary cell wall; lignin; *OsSWN1*

2016-P07

種子散布能力に関する果実二型をもつ海岸植物クサトベラ, —成熟段階ごとの果実形態の比較—

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Abstruct: *Scaevola taccada* is a coastal shrub species. This species has an unique characteristic that having two morphs of fruits adapted to two distinct dispersal modes. (1) C-morph fruits have pulp and cork layer and are dispersed by water and frugivorous birds and (2) NC-morph fruits have only pulp layer and are dispersed only by birds. This cork layer of C-morph fruit consists mainly of lignin. In order to identify the critical fruit developmental times of C-and NC-morph fruit, the developmental time of lignin deposition of the cork layer was studied by staining lignin with phloroglucinol-HCl solution and was observed with light microscope.

Keywords: fruit; dimorphism; lignin; seed dispersal

2016-P08

CRISPR/Cas9 システムを用いたコニフェルアルデヒド 5-ヒドロキシラーゼ機能欠損イネの作出

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Generation of a loss-of function mutant of *CONIFERALDEHYDE 5-HYDROXYLASE* gene in *Oryza sativa* using the CRISPR/Cas9 system

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Abstract: Aromatic composition of lignin greatly affects usability of lignocellulosic biomass and therefore has been one of the primary targets of cell wall engineering studies. We previously reported that RNAi-mediated down-regulation of a rice gene encoding CAld5H (OsCAld5H1) leads augmentation of G lignin units in rice cell walls. As G-rich lignins display higher calorific values than that of S-rich lignins, increase of G lignin units may contribute to enhancing combustion properties of biomass. On another front, the CRISPR/Cas9 genome-editing system has proven to be a powerful tool for efficient targeted mutagenesis. In this study, we attempted to generate *OsCAld5H1* knock-out mutant rice using the CRISPR/Cas9 system. Three single guide RNAs (sgRNAs) were designed to target distinct sites of *OsCAld5H1*, and incorporated into the Cas9-sgRNA expression vector. After *Agrobacterium*-mediated transformation, we obtained rice T_0 generation with anticipated mutations. The majority of the T_0 genotype, however, were chimeric or heterozygous for *OsCAld5H1* mutation. Plants homozygous for *OsCAld5H1* mutation were then successfully isolated from T_1 generation plants.

Keywords: lignin; *Oryza sativa*; coniferaldehyde 5-hydroxylase; ferulate 5-hydroxylase; CRISPR/Cas9 system

2016-P09

Transcriptional analysis of poplar CWPO-C in different cell types and organs

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Abstract: Cationic cell-wall-bound peroxidase (CWPO-C), a class III peroxidase in *Populus alba,* has been considered to play a role in the lignification process. In order to promote better understanding about CWPO-C functions, detailed expression analysis of this peroxidase using laser microdissection and expression quantification tools were performed. It was shown that cells did not express *CWPO-C* in cambium, but it did in cortex cells. Also *CWPO-C* expression was observed in apical meristem to some extent, thus indicating to be involved in growth and cell elongation; suggesting a new aspect to the role of CWPO-C.

Keywords: poplar; peroxidase; laser microdissection; gene expression; GUS reporter gene

2016-P10

ゼロから創製する新しい木質の開発

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New wood production in plant without wood formation

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Abstract: Plant cell wall, especially lignocellulose enriched in secondary cell wall, provides physical rigity and also has a large potential as a resource for the next-generation biofuel and biomaterials. However, its recalcitrance hampers the industrial use and therefore, the development of inovative technogy to improve it is desired. In this study, we expressed chimeric activators and chimeric repressors of ca. 300 transcription factors in *Arabidopsis nst1-1 nst3-1* double mutant, which lacks secondary cell walls in fiber cells, under the control of the *NST3* promoter. Some resultant transgenic plants reconstituted different cell wall from wild-type secondary cell wall like the striated cell wall similar to vessel element, abnormally and heavily lignified cell wall, and lignin-less cell wall in interfascicular fiber cells. Expression pattern of secondary wall associated genes and monosaccharide composition in these reconstituted lines were different from those of wild type even in the case when the reconstituted secondary cell wall looked similar to that in wild type, suggesting that these cell walls are reconstituted differently from wild type through partial activation of regulatory network of secondary cell wall formation. Using some factors identified in this screening, we successfully established the strategy to reinforce wood formation, that to produce easily-extractable cellulose, and that to produce cell wall without crystalline-cellulose. This study demonstrates that our approach is powerful to identify the novel transcription factors which regulates cell wall formation and also provides the potential tool to produce artificial tailor-made cell walls with novel traits for the biofuel and biomaterial production.

Keywords: Artificial cell wall; *nst1 nst3* double mutant; transcription factor; wood reinforcement.

2016-P11

Contribution of host lignin on haustorium induction and host defence against obligate parasitic plant *Striga hermonthica* and facultative parasitic plant *Phtheirospermum japonicum*

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Abstract: As one of major constitutes of secondary cell wall, lignins provide plants with physical strength and rigidity for maintaining proper structure and physiology. Meanwhile, lignins from host plants are also chemical targets for parasitic plants to find and attack host through formation of a specialized organ, named haustorium. The aim of this study is to understand to what extent host lignin compounds contribute to the formation of haustorium as well as host resistance against different parasitic plants. As a material, we used a facultative root parasite *P. japonicum* and obligate root parasite *S. hermonthica*. First, haustorium induction assay was performed by treating parasitic plants with monolignols, quinones and flavonoids. For both parasitic plants, H type monolignols are inactive whereas S type monolignols are active haustorium inducer. Interestingly, ferulic acid, which belongs to G type monolignol is active only in *S. hermonthica*. In addition, a flavonoid aglycon, peonidin induces haustorium only in *S. hermonthica*. These suggest that *S. hermonthica* has a broader spectrum of chemicals for haustorium formation. In parallel, host plants (Nipponbare rice) with altered ratio of G and S lignin composition were generated by genetic modification of F5H gene, which encodes ferulate-5-hydroxylase, a cytochrome P450-dependent monooxygenase (P450). These transgenic rice plants were tested for haustorium induction and host susceptibility/resistance assay in order to address the importance of G and S lignin composition in host plants with regard to host defense against parasitic plants. The reduction in S lignin in rice host resulted in decreased induction of haustoria in *P. japonicum*, and increased S lignin induced more haustoria. On the other hand, altered ratio of S and G lignin did not exhibit any difference of the haustorium induction against *S. hermonthica*. Unexpectedly, changed ratio of G and S lignin caused host plants more susceptible to *S. hermonthica* at the later stage of infection. In general, we found a consistency between in vitro and in vivo haustorium induction. Our study demonstrates a similar but yet parasite-specific perception of lignin compounds as haustorium inducer and highlight the importance of host lignin for parasitic plant infection.

Keywords: parasitic plant; haustorium; *Striga*; *Phtheirospermum*; host defense; lignin; cell wall

2016-P12

代謝工学的改変によるケイ皮酸モノリグノール経路の進化過程の考察

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Metabolic redesign of the cinnamate/monolignol pathway in *Marchantia polymorpha* by transgene expression of CYP98A3, CYP84A1, and hydroxycinnamoyl CoA transferase from Arabidopsis.

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Abstract: Comparison of genome sequences of *Marchantia*, *Physcomtrella*, and *Arabidopsis* revealed the presence of several key genes in the upstream part of cinnamate/monolignol pathway in the moss. Those include the cytochromes P450, cinnamate 4-hydroxylase (CYP73A) and *p*-coumarate 3'-hydroxylase (C3'H, CYP98A), and hydroxycinnamoyl CoA:shikimate/quinate hydroxycinnamoyl transferase (HCT) , while another downstream key enzyme CYP84A (F5H, ferulate 5-hydroxylase) is missing. We have expressed recombinant CYP98A (PpCYP98A) and HCT (PpHCT) from *Physcomitrella patens* and found that PpHCT catalyzes the higher plant type reaction with shikimate and quinate as the substrates. However, PpCYP98A failed to exhibit the C3'H activity with the PpHCT reaction products (e.g., *p*-coumaroyl shikimate). These results suggested that the endogenous substrates of the moss HCTs are different from those of the higher plant HCTs and that the moss CYP98A may assume unidentified roles aside from cinnamate/monolignol pathway. In other words, the evolution of the lignin biosynthesis could be understood, at least in part, through the speciation of CYP98A enzymes to be capable of C3'H reaction. If this was actually the case, transgene expression of the higher C3'H, F5H, and HCT from higher plants should have crucial impact on the moss metabolism stemming from phenylpropanoids. Here, we report the generation and characterization of transgenic *M. polymorpha* expressing *Arabidopsis* CYP98A3 (C3'H), HCT, and CYP84A1 (F5H) in different combinations.

Keywords: cinnamate/monolignol pathway, moss, evolution, cytochrome P450, metabolic redesign

2016-P13

フェニルプロペン香気成分の生合成に関わるモノリグノールアセチル化酵素遺伝子の単離と機能解析

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Isolation and characterization of monolignol acetyltransferase genes capable of biosynthesizing volatile phenylpropenes

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Abstract: Acetyl monolignols are key precursors for small molecular volatile phenylpropenes and macromolecular lignin in some plant species. Despite many previous investigations on the cinnamate/monolignol pathway, there are few reports regarding the isolation of monolignol acetyltransferases and the metabolic engineering of monolignol acetylation in plants. In this study, we searched monolignol acetyltransferase genes in a phenylpropene-producing plant, dill (*Anethum graveolens*). In addition, we overexpressed petunia (*Petunia hybrida*) coniferyl alcohol acetyltransferase (*PhCFAT*) with or without petunia *eugenol synthase* (*PhEGS*) in hybrid aspen. We found two candidate monolignol acetyltransferase genes in dill EST databases. The expression of a candidate gene was correlated with the accumulation of dill phenylproepenes, myristicin and dillapiole. In leaves of the aspen plants overexpressing *PhCFAT* and *PhEGS*, the amounts of eugenol and its glycoside increased up to 7-fold and up to 22-fold higher compared to wild type. Acetylated monolignol units were also significantly increased in the xylem of transgenics.

Keywords: phenylalanine, aromatic compound, herb, antifungal activities, phenylpropenes

2016-P14

Sphingobium sp. SYK-6株のシリンギル型リグニン由来化合物代謝に関わるアルデヒドデヒドロゲナーゼ遺伝子の同定と機能解析

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Identification and characterization of the aldehyde dehydrogenase genes crucial for the syringyl lignin catabolism in *Sphingobium* sp. strain SYK-6

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Abstract: *Sphingobium* sp. strain SYK-6 is capable of catabolizing various lignin-derived aromatics with guaiacyl and syringyl nuclei via vanillin (VN) and syringaldehyde (SN), respectively. An aldehyde dehydrogenase (ALDH) gene, *ligV*, essential for the conversion of VN was previously isolated from SYK-6, and genetically characterized. In this study, we aimed to identify the ALDH gene responsible for the conversion of SN from the 23 ALDH genes in SYK-6. All of these ALDH genes were expressed in *Escherichia coli*, and we found that nine gene products including LigV exhibited SN oxidation activity. Among these genes, SLG_28320 (*desV*) and *ligV* were transcribed in significantly higher levels in a constitutive fashion in SYK-6 cells. Disruption of *desV* in SYK-6 cells resulted in significant decreases in the ability to grow on and convert SN. The K_{cat}/K_m value of purified DesV measured for SN was 730-fold higher than that of LigV. These results clearly demonstrate that *desV* plays a main role in the conversion of SN in SYK-6.

Keywords: bacteria, benzaldehyde, genome, biorefinery, microbial lignin valorization

2016-P15

Sphingobium 属細菌のフェニルクマラン型化合物代謝に関与する lignostilbene α,β-dioxygenase 遺伝子の同定と機能解析

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Isolation and characterization of the lignostilbene α,β-dioxygenase genes involved in the catabolism of dehydrodiconiferyl alcohol in *Sphingobium* sp. strain SYK-6

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Abstract: The objective of this study is to identify and characterize all the *Sphingobium* sp. SYK-6 genes involved in the catabolism of a phenylcoumaran-type compound, dehydrodiconiferyl alcohol (DCA). In SYK-6 cells, the alcohol groups at the γ-carbon of the B-ring and A-ring side chains of DCA were oxidized in a sequential order to the carboxyl groups to generate DCA-CC. DCA-CC was decarboxylated to produce DCA-S, followed by the production of 5-formylferulate and vanillin by the cleavage of the Cα-Cβ double bond of the A-ring side chain of DCA-S. In a previous study, we isolated and characterized the genes involved in the conversion of DCA into DCA-CC. In this study, we investigated the genes responsible for the conversion of DCA-S. Previously, four lignostilbene α,β-dioxygenases (LSD) were reported as enzymes capable of converting DCA-S in *Sphingomonas paucimobilis* TMY1009. Here, we found eight LSD genes in the SYK-6 genome. Disruption of these genes in SYK-6 suggested that three *lsd* genes, *lsdB*, *lsdD*, and *lsdE*, play important roles in the degradation of DCA-S. These genes were expressed in *E. coli* and *Pseudomonas putida*, and the resultant gene products were purified by Ni-affinity chromatography. While LsdD converted DCA-S into vanillin and 5-formylferulate, LsdB and LsdE showed almost no activity toward DCA-S. These results may suggest that

LsdB and LsdE function as a heterodimer.

Keywords: dilignol, β-5, biodegradation, catabolic pathway

2016-P16

Sphingobium sp. SYK-6株におけるacetovanillone変換酵素遺伝子群の機能と転写制御

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Characterization of the acetovanillone catabolic genes and their transcriptional regulation in *Sphingobium* sp. strain SYK-6

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Abstract: In *Sphingobium* sp. SYK-6 cells, guaiacylglycerol-β-guaiacyl ether (GGE) is catabolized to vanilloyl acetic acid (VAA). It has been suggested that VAA was converted to vanillate through reactions that require coenzyme A. On the other hand, it is known that VAA is transformed to acetovanillone (AV) by nonenzymatic decarboxylation. Recently, we found that SYK-6 degraded AV via VAA, and the *acvABCDEF* genes, which respectively encode similar proteins of phenyl phosphate synthase 1, phenyl phosphate synthase 2, biotin carboxyl carrier protein, biotin carboxylase, carboxyltransferase, and sugar phosphatase of the HAD superfamily, were involved in the carboxylation of AV. In this study, we aimed to characterize the AV decarboxylase and the transcriptional regulation of the *acv* genes. Each *acv* mutant was incubated with AV, and their abilities to convert AV were examined. This experiment indicated that *acvA*, *acvB*, *acvC*, *acvD*, and *acvE* except *acvF* were essential for the conversion of AV in SYK-6. Due to the presence of *acvR*, which encodes an AraC-type transcriptional regulator, just upstream of *acvA*, AcvR seemed to regulate the transcription of *acvABCDEF*. Disruption of *acvR* in SYK-6 resulted in deficiencies in the growth on and the conversion of AV, suggesting that AcvR positively regulates the *acvABCDEF* transcription.

Keywords: bacteria, carboxylation, acetovanillone

2016-P17

海底下嫌気性微生物群集のリグニン関連モノマー代謝

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The metabolism of a lignin-related aromatic monomer by the anaerobic microbial community enriched from coal-bed below the seafloor

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Abstract: An enriched methanogenic community from ~2-km-deep coal-bed samples below the seafloor in the Pacific Ocean off Japan was examined for the metabolism of a lignin-related aromatic monomer, syringaldehyde, under an anaerobic condition. Syringaldehyde was converted into syring acid, and then into 5-hydroxy vanillic acid and gallic acid. Bacterial and archaeal community analyses showed the dominance of bacterium belonging to the three phyla, *Firmicutes* (class *Clostridia*), *Cloloflexi* (class *Anaerolineae*), and *Euryarchaeota* (class *Methanobacteria*, i.e. methanogenic archaea). This study will lead to a future understanding for unknown microbial metabolic networks for lignin-derived aromatic compounds under the seafloor.

Keywords: anaerobic degradation, *Clostridia*, *Cloloflexi*, aromatic monomer, methanogenic community, sub-seafloor,

2016-P18

海洋性細菌に由来するリグニンβ-*O*-4還元開裂酵素GST4の解析

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Analysis of β-*O*-4 cleaving enzyme, GST4, from the marine bacterium, *Novosphingobium* sp. MBES04

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Abstract: The deep-sea marine bacterium, *Novosphingobium* sp. MBES04, isolated from a sunken wood was capable of metabolizing the stereoisomers of β-*O*-4 lignin dimers into the respective monomers by combination of multiple enzymes. GST4 is a glutathione-dependent β-etherase, and one of the key enzymes in the pathway which selectively catalyzes reductive cleavage of β-*O*-4 aryl-ether bonds in lignin. In this study, we compared the substrate binding mechanisms of GST4 with its homologues of LigF from *Sphingobium* sp. strain SYK-6 and LigF-NA from *Novosphingobium aromaticivorans*. Substrate specificity analysis revealed that GST4 is capable to accept a wide range of substrates compared to the others. Calculation of energy for intermolecular interaction between the three molecules (GST4, glutathione and α-(2-methoxyphenoxy)-β-hydroxypropiovanillone (MPHPV)) suggested the substrate recognition of GST4 was determined by two different key rules of electrostatic interaction for glutathione and dispersion interaction for MPHPV.

Keywords: lignin, *Novosphingobium*, glutathione-dependent β-etherase, FMO

2016-P19

海洋環境からの Guaiacylglycerol-β-guaiacyl ether - Cα 位酸化酵素の探索

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Screening of guaiacylglycerol-β-guaiacyl ether – Cα-dehydrogenases from marine environment

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Abstract: A bacterial enzymatic cascade for β-*O*-4 reductive cleavage in lignin model dimers consists of Cα-dehydrogenases belonging to short-chain dehydrogenase/reductase (SDR) superfamily, β-etherases and glutathione-S-transferase (GST) superfamily, β-glutathione thioetherases (glutathione lyases). In this study, functional screenings of culturable bacteria isolated from sediments obtained from Kagoshima Bay revealed the existence of a bacterium with oxidative activity for hydroxyl moiety at Cα (benzyl) position of guaiacylglycerol-β-guaiacyl ether (GGGE). We conducted genome sequencing of the positive isolate designated as strain YG1 to identify responsible genes of the activity. Two genes encoding Cα-dehydrogenases were identified using recombinantly expressed proteins.

Keywords: β-*O*-4 reductive cleavage, a marine bacterium, guaiacylglycerol-β-guaiacyl ether (GGGE), *Sphingobium* sp., short-chain dehydrogenase/reductase (SDR)

2016-P20

リグノセルロース分解に関わる木材腐朽菌が産する酸化酵素の異種発現および構造活性相関解析

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Heterologous expression and structure-activity relationship analysis of the oxidative enzymes from wood rotting fungi that are involved in lignocellulose degradation

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Abstract: Fungi and their enzymes have been expected to provide milder means to extract lignin. By utilizing fungal enzymes and their functionally improved variants, more efficient use of lignocellulose may be achieved. We have selected several different ligninolytic enzymes registered in *Joint Genome Institute* (JGI) database and undertaken heterologous expression in *E. coli*. Three enzymes have been successfully expressed and purified in high yield with high stability and activity. The relationships between lignocellulose degradation and structure of these enzymes are under investigation. Our preliminary data shows that these three enzymes have different activity property.

Keywords: lignocellulose; wood rotting fungi; ligninolytic enzyme; heterologous expression

2016-P21

バイオマス細胞壁分解とオリゴ糖生成の促進に資する放線菌フェルラ酸エステラーゼ

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Streptomyces feruloyl esterase promotes enzymatic degradation of biomass and production of oligosaccharides

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Abstract: Feruloyl esterase (FAE) is useful to produce a ferulic acid from plant cell walls of agricultural biomass. Moreover, the FAE is one of important enzymes for degradation of plant cell walls in the process of biofuel production. In this study, we investigated an enhanced effect of *Streptomyces* FAEs (R18 and R43) to an enzymatic production of oligosaccharides and glucose from biomasses by carbohydrate-hydrolases, such as *Streptomyces* xylanase/cellobiosidase STX-I, *Streptomyces* α-L-arabinofuranosidase STX-IV and a commercial cellulase. By combining STX-I, STX-IV with R18 or R43, the contents of tri- to hexa-oligosaccharides that consist of hexose were increased from defatted rice bran and sugarcane bagasse. On the other hand, that of a di-oligosaccharide that consist of pentose was detected from corncob and sugarcane bagasse, and the di-oligosaccharide from corncob was obviously increased by the combination with FAEs. A combination of commercial cellulase with R18 or R43 increased glucose production from corn bran and corncob but did not enhance that from defatted rice bran and sugarcane bagasse. These results suggest that *Streptomyces* FAEs effect on cell wall degradation accompanying oligosaccharides and glucose production, and the recipe of enzymes is important for production of functional materials from various agricultural biomasses.

Keywords: cinnamic acid, feruloyl esterase, saccharification, biomass, *Streptomyces*

2016-P22

NMR study on lignocellulose degradation by *Coptotermes formosanus* Shiraki

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Abstract: Termites are effective in decomposing lignocellulose. Although degradation of polysaccharides components has been extensively studied, lignin degradation in lignocellulose digestion by termite yet remains unclear. In the present study, we applied modern NMR techniques to study lignocellulose degradation by a lower termite *Coptotermes formosanus* Shiraki with emphasis on the fate of lignin polymers. Softwood (Japanese cedar), hardwood (Japanese beech), and grass (rice) cell walls were fed to *C. formosanus*, and lignocellulosic structures of faeces and original dietary cell walls were comparatively characterized using 2D NMR techniques as well as various chemical methods. Our NMR and chemical analysis confirmed that polysaccharides were preferentially decomposed over lignins in digestion of all the three types of cell wall materials. However, it appeared that syringyl lignins were slightly depleted over guaiacyl lignins in digestion of beech cell walls. It was also clearly observed that guaiacyl lignins as well as tricin flavonoid units were depleted preferentially in digestion of rice cell walls. Distributions of major lignin inter-monomeric linkages were slightly affected but overall similar between faeces and original cell walls. Our data suggest that *C. formosanus* digestive system indeed removes part of lignin polymers along with polysaccharides upon lignocellulose degradation but most likely has little ability to exert major impact on the major lignin linkage types such as β–*O*–4, β–5, and β–β linkages.

Keywords: biodegradation, *Coptotermes formosanus* Shiraki, lignocellulose, NMR, termite digestive system

2016-P23

ラッカーゼ-メディエーター処理によるタイロシンの分解と毒性除去

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Degradation and detoxification of tylosin by laccase-mediator system

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Abstract: The adverse effect from the residual of pharmaceuticals and personal care products (PPCPs) in the wastewater on human health and the environment has become a matter of concern. Tylosin, a macrolide antibiotic, is used widely as a drug to treat infections for domestic animals, and it is found often as it is in several rivers and lakes all over the world. Considering the influences of tylosin to aquatic organisms, effective techniques to remove and/or to decompose it from wastewater have been demanded. To degrade and to detoxify tylosin, the treatments by laccese and laccase-mediator system with 1-hydroxybenzotriazole were examined. After treatment by laccase-mediator system, tylosin was not detected in the treatment solution, and the growth inhibitions against *Pseudokirchneriella subcapitata* and *Bacills subtilis* of the treatment solution were reduced significantly.

Keywords: ligninolytic enzyme, white rot fungi, bioremediation, laccase-mediator, PPCPs

2016-P24

^{13}C NMR 法による二量体モデル化合物分解機構の解析

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Degradation mechanism analysis of dimeric model compound using ^{13}C NMR

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Abstract: ^{13}C Labeled lignin dimeric model compound, a guaiacyl unit linked to a syringyl one by β-*O*-4 bond, was synthesized, and treated by laccase/1-hydroxybenzotriazole. Following the process of laccase-generated reaction by ^{13}C NMR, the oxidation at benzylic position and the cleavage of Cα–Cβ bond of dimeric model compound were observed. Veratric acid was determined as a reaction product, although it was not seen in the laccase-generated reaction solution of the oxidized dimeric model compound product as a substrate.

Keywords: dimeric model, ^{13}C NMR, laccase, bond cleavage, oxidation

2016-P25

Evaluations of antiviral activities of phenolic compounds in wood and bamboo vinegar toward production of lignin-derived bioactive compounds

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Abstract: Wood and bamboo vinegar (WBV), also called pyroligenous acid (PA), are made from smoke generated during the process of wood charcoal production. Over 200 compounds have been found in wood and bamboo vinegars, which belong to different classes of organic compounds, aldehydes, ketones, alcohols, organic acids, esters, derivatives of furan and pyran, phenolics, hydrocarbons, and nitrogen compounds. Anti-oxidation, anti-inflammation, and anti-microbial activities of PAs have attracted more and more attentions in the recent years1-2). It was suggested that phenolic compounds were responsible for anti-oxidation and anti-microbial activities. Viruses threaten human's health and cause huge economic loss. Therefore, it is urgent to find simple and economic methods to control the outbreaks of virus. In our previous work, we found that bamboo vinegar (BV) from moso bamboo inhibited EMCV replication significantly. Phenol was identified as a major antiviral compound in BV. In addition, acetic acid, which is the most abundant component in BV, showed synergistic effects with phenol on the antiviral activities3). In wood and bamboo PAs, versatile phenolic compounds are involved but their antiviral activities are not well studied. Therefore, this research aimed at elucidating antiviral activities of phenol derivatives involved in wood and bamboo PAs.

Keywords: phenolic compounds, antivirus, wood and bamboo vinegar, pyroligneous acid, picornavirus;

2016-P26

Isoamericanol A from *Jatropha curcas* seed extract shows anti-cancer activity on human breast cancer cell MCF-7 by induction of G2/M stage cell cycle arrest with prolonged treatment and disruption of regular spindle formation with short-term treatment.

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Abstract: Our study reports on the anti-carcinogenicity of isoamericanol A (IAA) as *Jatropha curcas* seed extract. The results showed that IAA is capable of inhibiting cell proliferation in a dose-dependent manner on the human cancer cell lines of MCF-7, MDA-MB231, HuH-7, and HeLa. The molecular mechanisms of prolonged 25μg/ml IAA treatment on MCF-7 were initially investigated with DNA-microarray analysis, flow cytometry, TUNEL assay, Western blot, and quantitative real-time PCR. The results showed increased expression of BTG2 (B-cell translocation gene 2, $p<0.05$), p21 ($p21^{WAF1/CIP1}$, $p<0.05$), and GADD45A (growth arrest and DNA-damage-inducible, alpha, $p<0.001$), in addition to decreased expression of CDK1 (cyclin-dependent kinase 1, $p<0.05$) and cyclins B1 ($p<0.001$) and B2 ($p<0.001$). These expressional changes indicate an inhibition of the cyclin B/CDK1 complex, the major activator of G2/M cell cycle progression, hindering further cancer cell growth. Later, we used immunofluorescence staining of aurora B kinase, α-tubulin, and the chromosome to test the effects of short-term IAA treatment on MCF-7. In comparison to the prolonged IAA treatments, we discovered that the short-term treatment impaired cell division by inducing irregular spindle forms. These findings suggest IAA could have the potential to halt cancer cell growth by at least two distinct mechanisms: G2/M cell cycle arrest and improper cell division.

Keywords: Neolignan; BTG2; $p21^{WAF1/CIP1}$; GADD45A; CDK1/cyclin B; mitosis

2016-P27

生物代謝による化学変換のためのリグニンの高温高圧水処理

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High-temperature liquid water treatment of lignin for chemical conversion through microbial catabolism

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Abstract: Lignin was treated by high-temperature liquid water using a semi-batch type reactor (218～290 ºC, 25 MPa, 3.0 g/min). The ethyl acetate-soluble products were analyzed by size exclusion chromatography (SEC) and gas chromatographic-mass spectrometric (GC-MS). As a result, lignin was degraded to low molecule weight products and was converted to phenolic compounds for microbial catabolism.

Keywords: hydrothermal, supercritical water, hot compressed water, SYK-6, vanillin

2016-P28

S 核、G/S 核 β-O-4 型オリゴマーの合成とその NHPI 間接電解酸化

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Synthesis and NHPI-mediated indirect electrochemical oxidation of S and G/S type β-O-4 model oligomer

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Abstract: Syringyl and guaiacyl/syringyl type β-O-4 model oligomers were newly synthesized (yields: 69.2, 78.9%, DP_n = 5.90, 5.32 on 1 g scale) and electrochemically oxidized in the presence of a redox mediator, *N*-hydroxyphthalimide (NHPI). Our NMR and GPC data suggested that α-positions of β-O-4 structure in both S and G/S-type oligomers were efficiently and selectively oxidized to the carbonyl group. Next, as a preliminary experiment for the subsequent reductive cleavage of α-keto-β-O-4 ether bond by electrochemistry, α-keto-β-O-4 type dimeric model compound was subjected to direct electrochemical reduction. We identified propiophenone derivative and guaiacol as the electrolysis products. This supports our contention that α-keto-β-O-4 ether bond could be reductively cleaved via direct electrolysis.

Keywords: β-O-4 linkage, C_α carbonylation, hardwood, lignin model compound, aryl ketone

2016-P29

第四級アルキルアンモニウムヒドロキシドを用いたリグニン分解におけるアンモニウムカチオンの役割

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Role of ammonium cations in degradation of lignin with quaternary alkyl ammonium hydroxides

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Abstract: In alkaline degradation of lignin, selectivity of the degradation toward low MW compounds, especially vanillin, is considerably improved by the presence of the tetrabutyl ammonium cation. In this presentation, we examined degradation of a non-phenolic β-O-4 type model compound in aqueous solutions of quaternary ammonium hydroxides having C1-C6 alkyl chains and NaOH. Selectivity toward vanillin became higher by the change of the cation from Na+ to NMe4+. Elongation of the alkyl chain from C1 to C6 made further improvements with similar performance being exhibited by the C3-C6 cations. Quantum chemical calculations on the ammonium cations indicated that the selectivity toward vanillin was inverse proportional to the positive charge localized on the methyl end of the cations, that hydrophobicity of the ammonium cation plays important roles in determination of the selectivity.

Keywords: degradation, quaternary ammonium, alkali, model compounds

2016-P30

テトラブチルアンモニウムヒドロキシド 30 水和物を用いたリグニン分解における各種添加剤の影響

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Influence of additives on degradation of lignin with tetrabutylammonium hydroxide-30H_2O

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Abstract: In tetrabutylammonium hydroxide-30H_2O ($NBu_4OH\cdot 30H_2O$), lignin is degraded selectively into low MW compounds, especially vanillin. This study addresses influence of several additives on the degradation of soda lignin in $NBu_4OH\cdot 30H_2O$. Two types of additives were tested: oxidants such as $PyClCrO_3$, $PyFCrO_3$, $NBu4ReO_4$, $NPr4RuO_4$, $NBu4ClO_4$, $(NBu4)_2SO_4$, $(NBu4)_2Cr_2O_7$ and nitrobenzene, and a H-donor, 2,4-dihydronaphthalene (tetraline). The oxidants greatly accelerated the degradation, but scarcely affected the maximum vanillin yield, suggesting that the property of $NBu_4OH\cdot 30H_2O$ advantageous for vanillin production was not exploited in the presence of the oxidants. On the other hand, tetraline considerably increased vanillin yield without affecting the reaction time necessary to achieve the maximum vanillin yield. This suggests that the effect of $NBu_4OH\cdot 30H_2O$ as a selectivity enhancer of vanillin was maintained in the presence of tetraline and the H-donor suppresses radical-induced side reactions.

Keywords: degradation, vanillin, oxidants, H-donors, tetrabutylammonium hydroxide

2016-P31

Copper complex-peroxide reaction producing vanillin from lignin in woody biomass accelerated by microwave

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Abstract: Vanillin and vanillic acid are degradation products from lignin and attract a great deal of interest as key components for synthesizing thermostable biopolymers. We investigated production of vanillin and vanillic acid from woody biomass, and found a microwave-accelerated copper-peroxide reaction producing these monomers in a high yield from woody biomass. In order to understand the mechanism for the microwave effect, the reaction was applied to lignin *β*-*O*-4 dimer model compounds, and the degradation products were analyzed comparatively using microwave irradiation and conventional heating.

Keywords: lignin, microwave, vanillin

2016-P32

疎水性アルコールを用いた植物バイオマスの効率的な成分分離法の開発

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Analysis of effect of alcohol addition to dilute acid pretreatment

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Abstract: Utilization of bioresource is important to reduce dependence on oil and greenhouse gas emissions. Lignocellulosic biomass is a renewable resource and mainly composed of cellulose, hemicellulose and lignin. Because lignocellulosic biomass has such complex structure, bioethanol production process requires pretreatment and enzymatic hydrolysis to liberate sugars for microbial fermentation. Especially, lignin was known as inhibitor of enzymatic hydrolysis. Therefore, removing lignin is important for realization of efficient biorefinery process. Previous study reported that alcohol pretreatment can remove lignin efficiently. But, alcohol pretreatment requires large amount of alcohol (30-50%). Because high amount of alcohol increase cost of biorefinery process, reduction in alcohol usage is required. In this study, small amount (12.5%) of six kinds of alcohol was added to dilute sulfuric acid pretreatment, and effect of alcohol for pretreatment was analyzed.

Keywords: organosolv pretreatment, fractionation, 1-butanol, lignin, cellulose

2016-P33

木材中の多糖/リグニンの混在スケールの評価

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Estimation of mixing scale for polysaccharide/lignin in wood.

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Abstract: Cellulose, hemicellulose, and lignin are the major components of wood. In general, distribution states of cellulose microfibril and lignin may significantly affect material and processing properties of wood. However, there is no standard measure to evaluate the deposition states. In the present study, we prepared the wood powders with the different polysaccharide/lignin ratios by ball milling and successive enzymatic hydrolysis, aiming to estimate the mixing states by adopting the procedures established for polymer blends. In this report, glass transition behavior of lignin component surrounding polysaccharide in hinoki-cypress wood flour (WF) was investigated using differential scanning calorimetry (DSC). The results revealed a systematic composition-dependent shift in the glass transition temperature (T_g) for the lignin component. The components in the WF can thus be regarded as in an intimate mixing state on a T_g -detection scale (20–30 nm).

Keywords: wood powder, glass transition, thermal analysis, enzymatic hydrolysis, segment motion

2016-P34

樹木細胞壁モデルを用いた木化の物理的寄与に関する研究

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Studies on the physical contributions of lignification using wood cell wall models

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Abstract: We used cellulose nanofiber hydrogels as a plant cell wall model and deposited artificial lignin models. This process was reproduction of lignification. Then the hydrogels made by such method were immersed in ethanol including coniferyl alcohol, peroxidase and H_2O_2. Dehydrogenation polymer (DHP) were synthesized in gels after evaporating ethanol under reduced pressure. As a result, it was confirmed that DHPs increased compression strength of gels. However, it was suggested that DHPs did not affect compression strength when amounts of DHPs was more than 20 % of cellulose.

Keywords: artificial lignification, cellulose nanofiber, dehydrogenation polymer, compression strength

2016-P35

改質リグニン製造システムにおけるリサイクル薬液のキャラクタリゼーション

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Characterization of the recovered PEG from the acid-catalyzed solvolysis system of the glycol lignin production

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Abstract: The acid-catalyzed solvolysis system of Japanese cedar using a glycol solvent as a solvolysis medium is being developed to produce a glycol solvent-modified lignin (glycol lignin) having thermal fusibility. A glycol solvent used as a solvolysis medium is recovered by removal of water from the supernatant of solvolysis liquor after glycol lignin precipitation, and reused in next production line. In this study, the solvolysis medium, polyethylene glycol (PEG), was recovered under several different recovery conditions and characterized by size exclusion chromatography, brookfield viscometer and moisture analyzer in order to develop a recycle system of a solvolysis medium. The molecular weight of the recovered PEG obtained from the improved recovery process was almost same as that of fresh PEG, whereas the viscosity of the recovered PEG was 1.4-fold higher than fresh PEG. It was found that the recovered PEG also showed a similar solvolysis reactivity to that of fresh PEG.

Keywords: acid-catalyzed solvolysis, glycol lignin, polyethylene glycol (PEG), solvent recovery, softwood

2016-P36

分析的熱分解法による酸加溶媒分解スギリグニンの構造解析

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Structural characterization of polyethylene glycol solvolysis lignin prepared from Japanese cedar by analytical pyrolysis

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Abstract: The acid catalyzed solvolysis of Japanese cedar was carried out using polyethylene glycol (PEG) as a solvolysis reagent in the presence of a very small amount of sulfuric acid (H_2SO_4) to isolate lignin fraction (PEG-lignin). PEG lignin were analyzed by the pyrolysis gas chromatography mass spectrometry (Py-GC/MS). A few pyrolysis products which were observed from PEG-Pulp and Japanese cedar were not observed from PEG-lignin. It suggests that β-O-4 linkage is minor structure of PEG-lignin. PEG content determined by PyGC/MS were 6.6-10.3%.

Keywords: PEG-lignin, pyrolysis gas chromatography/mass spectrometry, PEG content

2016-P37

pH-induced sequential fractionation and characterization of glycol lignin produced by acid-catalyzed polyethylene glycol (PEG) solvolysis of softwood

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Abstract: pH-induced sequential fractionation of alkali diluted solvolysis liquor obtained from acid-catalyzed PEG solvolysis of softwood meal was conducted to produce glycol lignin (GL) with different molecular weight and thermal flow properties. It was found that the larger molecular weight fraction (F1) was obtained at basic pH (pH8) and decreased gradually (F2> F3>F4) to acidic pH (pH2) at all PEG solvolysis systems. The solid GL fraction of >60% was collected at the first stage fractionation at pH8 in PEG200 solvolysis process, whereas the similar amount of solid GL fraction of >25% was obtained at pH8 (F1), pH6.5 (F2), and pH4.5 (F3) in PEG600 solvolysis process. As a result, the thermal flow property and thermal stability of GL fractions varied accordingly.

Keywords: glycol lignin, polyethylene glycol (PEG), acid-catalyzed solvolysis, fractionation, thermal flow behavior

2016-P38

アセチル化アルコリシスリグニン及びこれを硬化剤とするエポキシ樹脂硬化物の合成と熱的性質

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Synthesis and thermal properties of acylated lignin and epoxy resi cured with acylated lignin

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Abstract: Cured epoxy resins were prepared using acetylated alcoholysis lignin (AcAL). AcAL was synthesized by a reaction of AL with isopropenyl acetate in the presence of catalytic amount of *p*-toluenesulfonic acid. Bisphenol A diglycidyl ether (BPADGE) and a catalytic amount of 2-ethyl-4-methylimidazole (2E4MI) were dissolved in tetrahydrofuran (THF), and then THF was removed under a reduced pressure. The obtained reaction mixtures having a [EPOXY]/[PhOAc] mole ratio of 1.0 was cured at 180 ºC for 5 hr. Thermal properties of the obtained cured epoxy resins were studied by differential scanning calorimetry (DSC) and thermogravimetry (TG). It was found that AcAL can be synthesized using isopropenyl acetate and that the curing reaction between PhOAc groups of AcAL and epoxy groups of BPADGE occurs under the appropriate curing conditions.

Keywords: epoxy resins, acetylated lignin, synthesis, thermal properties

2016-P39

脱メチル化リグニンの調製と機能性評価（その2）

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Demethylation of G/S and S-type dehydrogenation polymers (G/S, S-DHP)

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Abstract: To upgrade lignin, demethylation of guaiacyl and syringyl-type dehydrogenation polymers (G/S-, S-DHP) with iodocyclohexane were carried out. HSQC NMR spectra of the demethylated DHPs proved that demethylation proceed smoothly. The result was supported by Phenolic-OH content of demethylated DHPs. Demethylated S-DHP had higher iron adsorption and Bovine Serum Albumin (BSA) adsorption abilities than demethylated G/S-DHP, although it had similar DPPH radical scavaning ability to demethylated G/SDHP.

Keywords: lignin, tannin, iodocyclohexane, demethylation, HSQC NMR

2016-P40

木質バイオマスの分子構造変換によるブロックコポリマーの調製とナノ粒子化

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Lignin based-block copolymer and its nano particles from woody biomass

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Abstract: Sawdust from Japanese Larch (*Larix leptolepis*) was methylated or acetylated, and subsequently fractionated by solvent extraction. Methylated and acetylated fractions were azido- or alkyne-functionalized via Lewis acid catalyzed depolymerization. Cellulose and lignin-based block copolymers were synthesized via Huisgen 1,3-dipolar cycloaddition between methylated and acetylated fractions, followed by the removal of acetyl groups. Chloroform solutions of the block copolymers were spray dried to afford their nano particles.

Keywords: organic Qdot, tetrabutylammonium fluoride trihydrate, 1-ethyl-3-methylimidazolium acetate, benzyl methyl ether, hemicellulose

2016-P41

変性草本系リグニンを用いた高性能フェノール樹脂

木村 肇1)、大塚 恵子1)、米川 盛生1)、松本 明博1)、谷口 勇希2)、山本 麻衣子2)、周 霖2)、大橋 康典2)
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High performance phenolic resin based on modified herbaceous lignin

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Abstract: In this study, we intended to develop the high performance phenolic resin based on natural herbaceous lignin and revealed the characteristics. Generally, though natural lignin is added simply to phenolic resins, for reactivity with the thermal fluidity of lignin is low, modification by lignin does not proceed sufficiently. Therefore, modified herbaceous lignin which was reactive to phenolic resins was prepared and the properties of the phenolic resin based on modified herbaceous lignin were investigated. The properties of the phenolic resin with modified herbaceous lignin were estimated by heat resistance, mechanical property, electrical insulation and water resistance and compared to the phenolic resin with usual herbaceous lignin or without lignin. As a result, it was revealed that the phenolic resin with modified herbaceous lignin showed good heat resistance, mechanical property and electrical insulation.

Keywords: lignin, herbaceous, phenolic resin, benzoxazine, heat resistance

2016 ワークショップ－企画講演：リグニンの最新像と関連分野との連携－
第一部：NMR 法で見えてきたリグニンの最新像（W1～W3）

2016-W1

解析法の概要と樹木リグニンの化学構造的特徴

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Structural characteristics of softwood and hardwood lignins and their analytical methods

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Abstract: The developments of NMR spectroscopy and the lignin NMR database have provided new insights in the field of lignin chemistry filed. Dibenzodioxocins and spirodineones, those are the structural units relatively newly proposed in softwood and hardwood lignins, can be seen on ^{1}H-^{13}C 2D NMR spectra of lignin. As well as NMR methods, chemical degradation methods also play important roles on the structural elucidation of lignins since they have some advantages over the NMR methods, and vice versa. Structural characteristics of softwood and hardwood lignins and their analytical methods will be shortly introduced in this presentation.

Keywords: β–O–4, resinol, phenylcoumaran, β–1, biphenyl

2016-W2

多様性と可変性：草本リグニン、種皮リグニン、組換え植物リグニン

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Lignin diversity and flexibility: lignins in grasses, seedcoats, and transgenic plants

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Abstract: Extensive studies on the structure of lignin using advanced NMR techniques have revealed the substantial diversity and flexibility of the polymer's assembly in nature. It is becoming increasingly evident that the structure and biosynthesis of grass lignins are substantially different from those of hardwood/softwood lignins; besides typical monolignols in hardwoods and softwoods, i.e., coniferyl and sinapyl alcohols, grass lignins uniquely incorporate γ-*p*-coumaroylated monolignols as well as a flavonoid tricin upon lignification. Recently discovered catechyl-type lignins derived from caffeyl and 5-hydroxyconiferyl alcohols in dicot and monocot seedcoats exemplify the flexible – but yet substantially organized – manner in which different lignin monomers are generated for lignification in different tissues/cells. Such flexibility of lignification is further illustrated by numerous examples of lignins in transgenics and mutants that incorporate various "unusual" lignin monomers that have arisen as a consequence of disruptions in the monolignol biosynthetic pathway.

Keywords: Gramineae, Poaceae, benozodioxane, CAD, CCR, CCoAOMT, COMT

2016-W3

リグニン—多糖複合体の解析と定量２次元 NMR 法

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Analysis of lignin–carbohydrate complex and 2D–NMR for quantification

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Abstract: Recent advances in NMR analysis give a better understanding of lignocellulose structures including lignin-carbohydrate complex (LCC), a key component connecting hydrophilic and hydrophobic macromolecules in plant cell walls. Several types of covalent linkages between lignin and hemicelluloses have been reported. These include α ether, α ester, γ ester, phenyl glycoside, and acetal bonds. 2D-NMR is a powerful tool to unveil the structure of LCCs, but it was difficult to obtain direct evidence for the LC linkages by NMR due to their very low frequency in cell walls. We concentrated LC linkages by enzymatic saccharification and adsorption chromatography, and the LCC fragments obtained were analyzed by long-range correlation NMR such as ^{1}H–^{13}C HMBC and HSQC-TOCSY in addition to HSQC. We also developed a new quantitative 2D-NMR named TAF (tolerant of any factors) which is tolerant of any factors such as variation in molecular size, the $^1J_{\mathrm{CH}}$ values, the presence of homonuclear ^{1}H–^{1}H couplings, and imperfections in NMR pulses.

Keywords: lignin-carbohydrate linkage, LCC, benzyl ether, quantitative NMR, Q-HSQC

2016 ワークショップ ー企画講演：リグニンの最新像と関連分野との連携ー
第二部：関連分野からの話題提供(W4～W6)

2016-W4

カスパリー線の機能と形成

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Function and formation of Casparian strip

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Abstract: The Casparian strip (CS) is a lignin-based cell wall modification deposited in the anticlinal wall of root endodermal cells. The CS prevents apoplastic flow of water and solute into the vascular system, making possible selective nutrient loading by transporters at the endodermis. However, molecular mechanisms of CS formation and its function in solute transport are unclear as no gene had been identified until recently. Through the analysis of mutants that have defects in nutrient transports, we have identified genes required for CS formation. One of the mutant has mutation in a transcription factor, MYB36. MYB36 directly upregulates expression of genes important for the correct formation of the CS domain and the localization of the CS biosynthetic machinery. The other mutant, *low-calcium sensitive 2* (*lcs2*), has been identified as a mutant whose growth was inhibited under low Ca condition. *lcs2* has mutation in a novel gene with unknown domain. *lcs2* has defect in CS formation and showed altered localization of CASP1, a gene required for correct localization of CS biosynthetic machinery, suggesting that *lcs2* is required for the correct localization of CASP1. Recently, through the analysis of these mutant, we reveal that defect of CS as a apoplastic barrier is complemented by suberin, a glycerolipid polymer. Our findings suggest the presence of the mechanisms for the coordinated formation of lignin and suberin.

Keywords: Casparian strip, cell wall, apoplast, suberin

2016-W5

リグニン由来含芳香族化合物群を利用した新規樹脂素材開発

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Development of novel polymeric materials utilizing aromatic chemicals from lignin

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Abstract: By using vanillin derivatives, the syntheses of aromatic polyesters, polyurethanes, and polyamides were carried out. Taking account of decomposition temperature of monomeric compounds, the polymerization conditions were optimized. As a result, the polyesters containing vanillin derivatives were obtained at high molecular weights (Mw>50,000). The obtained polyester had a melting temperature over 190 ºC and could be molded as a film specimen. When the drawing treatment was applied for the polyester films, the stretched films showed excellent mechanical properties as 120 MPa of tensile strength and 4.3 GPa of Young’s modulus. Furthermore, we succeeded in syntheses of novel polyurethanes from vanillin derivative and lysine-based diisocyanate. The polyurethanes from monomeric vanillin derivative as a sole diol component became to be hard resins with glass transition temperature around 70 ºC, whereas a mixing of alkanediol with vanillin derivative yielded soft polyurethane resins with elongation break over 500 %. The obtained polyurethanes were amorphous polymers and revealed very transparent characteristics as total light transmittance of over 90%. When the dimeric monomer of vanillin derivatives was used as a diol component, the obtained polyurethane became to be semi-crystalline polymer and had a melting temperature of 162 ºC and a glass transition temperature of 102 ºC. Thus we found that the thermal stability of polyurethanes could be improved by the imparting the symmetric structure to monomeric units. We also embarked on the synthesis of novel bio-based aromatic acrylic resins from cinnamate derivatives. The organic acids such as super strong acids catalyzed the group transfer polymerization of cinnamate derivatives at a C-C double bond to give the corresponding polymer molecules. Under the optimized conditions, the reaction yielded polymers of cinnamate derivatives with relative high molecular weights (M_w>30,000). The obtained polymers had higher glass transition temperature of 165 ºC, and the values were comparable to that of common petrochemical engineering plastic of polycarbonate.

Keywords: vanillin derivatives, aromatic polyesters, aromatic polyurethanes, cinnamate derivatives, aromatic acrylic resins

2016-W6

国産草本繊維質を用いた糖質プラットホーム構築に向けた技術開発 ～現状と新たな挑戦～

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Current situation and new challenges of technology development for the sugar platform using domestic fibrous feedstocks

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Abstract: Sugar platform for lignocellulosic feedstock is highly expected as an environmentally-friendly process for production of fuels or chemicals, leading us to sustainable co-existence and co-prosperity of a new bio-business with rural agriculture/forestry. Recently we developed a “simple” sugar production system for domestic herbaceous biomass in Japan (rice straw and cellulosic energy crops as main feedstock) with an alkali pretreatment, termed the CaCCO (Calcium Capturing by Carbonation) process. In this paper, the simplicity of the CaCCO process as well as its improvement for various applications in rural areas is presented.

Keywords: sugar platform, CaCCO (Calcium Capturing by Carbonation) process, herbaceous feed stock, pretreatment, bioeconomy.

2016 ワークショップ　ーリグニン科学の基礎講座ー(W7～W9)

2016-W7

細胞壁の木化

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Lignification of cell wall

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Abstract: Lignification starts at cell corner middle lamellae when the secondary wall formation starts, and then proceeds to compound middle lamellae. Lignification of secondary wall starts at the outer portion, and proceeds toward the lumen lagging behind the cell wall thickening. Non-lignified secondary cell wall shows parallelly oriented cellulose microfibrils with many cross-linkings composed of hemicelluloses. When the lignification proceeds, many globular structures appear along the microfibrils. Monolignols are synthesized in the cell, transported toward the cell wall, and polymerized within the cell wall. Detailed process is discussed.

Keywords: basic course, cell wall, differentiating xylem, lignification, monolignol

2016-W8

リグニンとは　ー化学構造と単離リグニンー

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What is lignin?　ーChemical structure and isolated ligninsー

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Abstract: Lignin is an aromatic substance which comprises approximately 15-35% of the components of wood and other lignocellulosics. In this course, chemical structures of lignins, which vary depending on the taxonomical group, are introduced in terms of the composition of biosynthetic monomers and their radicals formation followed by radical coupling reactions. Types of lignin preparation method and characteristic features of isolated lignins are also briefly explained.

Keywords: basic course, chemical structure, linkage type, lignin preparations

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2016-W9

リグニンの化学分析法

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Chemical analysis of lignin

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Abstract:
Lignin-content determination
Klason method, Acetyl bromide method, Thioglycol lignin method, Kappa number test
Lignin chemical structure analysis
IR method, NMR method, Alkaline-nitrobenzene oxidation method, Thioacidolysis method, DFRC method and so on

Keywords::basic course, characterization, content, qualitative analysis, quantitative analysis, spectral analysis

第62回（2017.10.27-28）名古屋大学 野依記念学術交流館

207-101

木化に及ぼすヘミセルロースの影響

古川貴大1)、吉永新2)、高部圭司2)、松尾朱実3)、玉井裕4)、幸田圭一4)、浦木康光4)
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Effect of hemicelluloses on lignification

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Abstract: We have already examined xylan functions on the formation of dehydrogenation polymer (DHP) using artificial wood cell wall1). As results, xylan can introduce coniferyl alcohol as a monolignol into cellulose, and enhances the frequency of aryl ether linkage in DHP. In this study, we investigated glucomannan function as another typical hemicellulose through the same experiment as that for elucidation of xylan function. Glucomannan was adsorbed on bacterial cellulose film (BC) in much larger amount than xylan did. However, only trace of DHP deposition inside glucomannan-deposited BC film was determined by acetyl bromide method. Therefore, it is likely that glucomannan does not have similar functions on DHP formation to those of xylan.

Keyword: *dehydrogenation polymer (DHP), glucomannan, xylan, wood cell wall, lignification*

2017-102

Stereo-preferential formation of *p*-hydroxyphenyl-type β-O-4 structures from the quinone methides

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Abstract: A model experiment mimicking the *erythro*/*threo* (E/T) ratio determining-step for the formation of *p*-hydroxyphenyl-type β-O-4 structure during lignin biosynthesis was performed to investigate the effect of aromatic ring type on the E/T ratio. Four types of quinone methides (QM) were synthesized from corresponding β-O-4 dimer models carrying *p*-hydroxyphenyl (H)-and/or guaiacyl (G)-units [HH-, GH-, HG- and GG-type models (ex. GH-type: guaiacylglycerol-β-*p*-hydroxyphenyl ether)]. The water addition to the QMs was examined in different buffer conditions (pH 3-7). The *threo*-preferential formation was observed, but the *erythro*-preferential formation assumed based on the previous study of compression wood was not found in any QMs under any pH conditions. The E/T ratio of the β-O-4 dimers tended to be lower at a higher pH condition. At any pH, the *threo*-selectivity was always higher in the order of HH-＞GH-＞HG-＞GG-type of QM, indicating that *threo*-preferential formation was enhanced by the presence of H unit either as QM moiety or as etherified aromatic ring.

Keywords: quinone methide; β-O-4 structure; *p*-hydroxyphenyl; *erythro*/*threo* ratio; softwood lignin.

2017-103

植物細胞壁の木化におけるモノリグノールグルコシドの挙動と役割— Glycone 部（Glucose）の役割・命運について—

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Behavior and role of monolignol glucosides in lignifying plant cell walls
— Role and fate of glycone moiety (glucose) —

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Abstract: Monolignol glucosides are intermediate compounds in lignin biosynthesis. In the lignifying cell wall, monolignol glucosides are hydrolyzed by β-D-glucosidase into aglycone moiety, monolignols; *p*-hydroxycinnamyl alcohol, coniferyl alcohol and sinapyl alcohol, and glycone moiety, D-glucose (Glc). The aglycone moiety, monolignols are known to polymerize in the previously deposited polysaccharides gel to form macromolecular lignin-polysaccharides complexes. On the other hand, fate of the liberated D-glucose is not yet known. In this work, coniferins ^{13}C-enriched at aglycone and glycone moieties, coniferin-[side chain-^{13}Cα] and coniferin-[Glc-$^{13}C_6$] respectively, were administered to growing shoots of *Ginkgo biloba*, and fate of the Glc-[$^{13}C_6$] was traced in comparison with the fate of coniferyl alcohol-[side chain-^{13}Cα]. The side chain ^{13}Cα-enriched coniferyl alcohol moiety incorporated into lignin at expected level, around 4-5 % of the total lignin, due to dilution by the large flow of original lignin formation in the cell wall. On the other hand, a part of the liberated glycone moiety, Glc-[$^{13}C_6$], was incorporated into cell wall polysaccharides. Some part is supposed to be utilized for production of active oxygen species necessary for polymerization of monolignols, and some part for modification of polysaccharide structure in the later formation stage of lignin-polysaccharide complexes in the cell wall.

Keywords: ^{13}C-tracer method, δ^{13}C, alditol acetate, glucuronic acid, xylan

2017-104

イネにおける *p*-クマロイル-CoA モノリグノールトランスフェラーゼの酵素機能解析ならびに機能欠損変異株の作出と性状解析

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Functional analysis of *Oryza sativa p*-coumaroyl CoA:monolignol transferases and characterization of the knock-out mutants

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Abstract: Grass lignins are uniquely γ-acylated by *p*-coumaroyl residues which arise from the polymerization of γ-*p*-coumaroylated monolignols upon lignification. Currently, however, little is yet known regarding the biological origin, functions as well as any potential impacts on the biomass properties of such lignin γ-acylations in grass. Here, we describe our attempt to generate rice mutants deficient in *p*-coumaroyl-CoA:monolignol transferase (PMT) genes involved in the biosynthesis of γ-*p*-coumaroylated monolignols in rice. We identified two rice PMT candidates displaying the anticipated monolignol acylation activity *in vitro*. We then generated rice mutants deficient in the two PMT genes using CRISPR/Cas9-mediated targeted mutagenesis, and subjected their cell wall tissues to an in-depth structural analysis using 2D NMR.

Keyword
Lignin, Bio-refinery, *Oryza sativa* , *p*-Coumaroyl-CoA:monolignol transferase, CRISPR/Cas9 system

2017-105

Altered cell wall structure and improved biomass digestibility in tricin-truncated rice mutant deficient in flavone synthase II

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Abstract: A wide range of grass species utilize tricin flavone as a natural lignin monomer. However, the biosynthetic origin of tricin-bound lignin as well as the impacts of its manipulation on cell wall structures and properties remain poorly understood. This study addresses in-depth cell wall analysis on a tricin-trancated rice mutant deficient in a flavone synthase II (FNSII). A series of cell wall structural analyses using chemical and NMR methods demonstrated that the mutant produces lignins being completely devoid of tricin and incorporating naringenin as a novel flavonoid component. The mutant was further revealed to display enhanced enzymatic saccharification efficiency. Overall, we contemplate that manipulation of tricin biosynthetic pathway could be an alternative strategy for improving cell wall digestibility in grass crops.

Keywords
Lignin, *Oryza sativa*, Flavone synthase II, Tricin, Enzymatic saccharification

2017-106

選択的 ^{13}C 標識法と固体 NMR を用いた HG-DHP の構造解析

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Structural analysis of HG-DHP by ^{13}C-enrichment technique and solid-state NMR

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Abstract: In order to analyze lignin structures, ^{13}C-enriched HG-DHP made from the selective ^{13}C-enriched *p*-glucocoumaryl alcohol and unenriched coniferin was analyzed by solid-state ^{13}C CP/MAS NMR and two dimensional (2D) ^{13}C-^{1}H correlation HETCOR. Making difference NMR spectra between the ^{13}C-enrihed HG-DHP and unenriched HG-DHP provide simple spectra from the specific ^{13}C-enriched carbons. From the simplified differential spectra and HETCOR spectra of HG-DHP, we assigned the C3 and C5 chemical shift of lignin major structures involved in *p*-hydroxyphenyl unit (H unit), respectively.

Keywords: selective ^{13}C-enrichment, solid-state NMR, *p*-hydroxyphenyl unit (H unit), DHP

2017-107

分子運動性解析による多糖/リグニンのナノスコピックな共存形態の評価

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Evaluation of nanoscopic coexistence states of polysaccharide/lignin in lignocellulosic biomass by molecular mobility

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Abstract: Cellulose, hemicellulose, and lignin are the major components of wood. Information on these coexistence states in nanoscale is essential for promoting the effective use of wood and wood polymers. We aimed to evaluate nanoscopic average compactness of polysaccharide/lignin by differential scanning calorimetry (DSC) analysis and proton spin-lattice relaxation times in the rotating frame ($T_{1\rho}^{H}$) by solid state NMR. The DSC thermograms showed a systematic composition-dependent shift in the glass transition temperature (T_g) for the lignin component. The components in both samples can thus be regarded as in an intimate mixing state on a T_g-detection scale (20–30 nm). We also investigated the dependence of proton spin-lattice relaxation times in the rotating frame ($T_{1\rho}^{H}$) measured by solid-state NMR on the polysaccharide/lignin ratios and species. As a consequence, the enzymatically hydrolyzed samples showed an increase in the $T_{1\rho}^{H}$ value for the lignin component.

Keywords: Wood flour, Glass transition, solid-state NMR, Ball-milling, Enzymatic hydrolysis

2017-108

塩基性下におけるリグニン *β-O*-4 結合開裂反応に及ぼすカウンターカチオンの影響

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Effect of counter cation on the lignin *β-O*-4 bond cleavage under basic conditions

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Abstract: The *erythro* isomer of a non-phenolic *β-O*-4 lignin model compound, veratrylglycerol-*β*-guaiacyl ether (VG-*e*), was reacted in a H_2O solution, aqueous methanol solution, aqueous ethanol solution, or aqueous 1,4-dioxane solution containing LiOH, NaOH, or CsOH as a base under pulping conditions to examine the effect of the counter cations on the pulping reactions. The disappearance rate of VG-*e* was in the order of: CsOH > NaOH > LiOH, which presumes that Li^+ interacts with HO^- and suppresses the action of HO^- most significantly. A major reaction product, the *erythro* isomer of veratrylglycerol, was obtained with the highest yield, when CsOH was employed in each solvent system. This result suggests that the nucleophilicity of HO^{-} is sensitive to strength of the interaction between a counter anion and HO^{-}.

Keywords.
Alkyl-aryl ether, Alkali, Cooking, Wood

2017-109

リグニンの分子構造変化に伴う材色の変化

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The relationship between structural change of lignin and color characteristic of woods

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Abstract: Lignin is the main component of secondary cell walls in land plants. Occasionally, structural changes of the lignin are accompanied with a change in color of woods. Woods deposited in some of the mutants and transgenic plants with modified the lignin structures have different colors compared to wild-type plants, suggesting the color of woods is the one of good indicators for the lignin structural change. In this study, we characterize the structure of the lignin deposited in red-colored woods in a mulberry mutant we have recently recognized. The results from staining assay and monomeric composition analysis of the lignin in addition to that from lignin content analysis of the mutant will be presented.

Keywords: cinnamyl alcohol dehydrogenase, derivatization followed by reductive cleavage procedure, thioacidolysis

2017-201

Kinetic studies of the two fungal glutathione-dependent enzymes and their potential roles in the intracellular detoxification and wood-derived compound metabolism

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Abstract: Lignin, one of the wood components, is becoming important as a raw material when sustainable bio-refinery is concerned. However, it is highly complex and recalcitrant, thereby undervalued and underdeveloped. Wood decaying fungi have developed a complex enzymatic system and possess intracellular networks to deal with potential recalcitrant organic compounds. Glutathione-dependent enzymes are multifunctional and capable of catalyzing the detoxification reactions, tempting us to think that some of them, if not all, might be involved in wood-derived compound metabolism. In this study, we developed *Escherichia coli* expression systems for two fungal glutathione-dependent enzymes, individually, and successfully purified using affinity and size exclusion column chromatographies. Three model substrates were used to determine the activities involved in the intracellular detoxification. For wood-derived compound metabolism, three fluorescent compounds have been used to examine etherase and esterase activities. Our data strongly suggest that these two enzymes have distinct roles in both the fungal detoxification system and wood compound metabolism.

Keywords: fungi, glutathione-dependent enzymes, detoxification, metabolism

2017-202

白色腐朽菌ヒラタケにおける GH10・GH11 の機能喪失がリグニン分解に及ぼす影響について

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Effects of targeted disruption of genes encoding GH10 and GH11 on lignin degradation in the white-rot fungus *Pleurotus ostreatus*

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Abstract: White-rot fungi efficiently degrade wood lignin, and its mechanism remains to be elucidated. Lignin and carbohydrates form complex structures in wood. It was reported that a covalent linkage exists between lignin and hemicellulose via glucurono acid in beech wood, which suggests degradation of lignin can be affected by xylan. Various transcriptome and secretome studies were conducted in white-rot fungi, and it was shown that CAZys but not so many ligninolytic enzymes were responsive to lignocellulosic substrates. In this study, we examined the effects of targeted disruption of genes encoding GH10 and GH11 on lignin degradation in the white-rot fungus *Pleurotus ostreatus*, which intriguingly revealed that targeted disruption of one of GH11 genes decreased ability to degrade lignin in beech sawdust.

Keywords: *Pleurotus ostreatus,* targeted gene disruption, heterologous expression, xylanase, lignin degradation,

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2017-203

キノコによる木質リグニン分解と有性形態形成との間に、関係性はあるのか？

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Do the regulation mechanisms of wood lignin biodegradation coordinate with those of sexual development ?

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Abstract: Most wood decaying fungi belong to agaricomycetes, which are characterized by their dramatic morphological differentiation, fruiting development or mushroom formation. Fruit bodies are relatively large multicellular structures formed during sexual reproduction. Among wood decaying fungi, white-rot fungi play an important role in the global carbon cycle because they the species that almost exclusively degrade plant cell wall lignin in nature. Some previous studies suggested that there are some correlations/coordination between sexual reproduction and ligninolysis in some white rot fungi. It was recently shown that mutations that cause significant defects in the ligninolytic activity also cause defects in fruiting initiation in *Pleurotus ostreatus*. In this study, we investigated this hypothesis by extensive molecular genetics and genomic studies.

Keywords: white rot, fruiting development, mushroom, gene regulation

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2017-204

マンガンペルオキシダーゼ/複合メディエーター系によるリグニン分解機構の解析

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Analysis of lignin degradation mechanism by manganese peroxidase / complex mediator system

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Abstract: In this study, we attempted to construct the method of effective enzymatic delignification with manganese peroxidase (MnP) from beech wood. Ball mill treatment of wood meal was increased delignification efficiency of MnP/multi radical mediators reaction system, lignin degradation was reached at 10.6% for 48 hour reaction. And sequential enzymatic delignification slightly increased lignin degradation ratio to 13.5%. Because lignin degradation was reached sufficient level for structural analysis, at first alkaline-nitrobenzene oxidation was performed. By comparison for raw beech wood meal, recoveries of syringaldehyde and vanillin from enzymatic delignified wood were roughly 20% reduced. This result suggested that MnP/multi mediators system oxidized the non-condensed structure selectively, regardless to syringyl and guaiacyl type structure.

Keywords: *Phanerochaete sordida* YK-624, manganese peroxidase, lignin degradation, radical mediator, alkali nitrobenzene oxidation

2017-205

イオン液体触媒を利用したリグノセルロース系バイオマスのエステル交換反応におけるリグニン水酸基の反応性

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Transesterification Reaction of lignocellulosic Biomass using Ionic Liquid Catalyst: Reactivity of Hydroxyl Groups of Lignin

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Abstract: Polysaccharide acetate and lignin acetate were simultaneously synthesized from lignocellulosic biomass *via* transesterification with isopropenyl acetate (IPA) as an ester donor in an ionic liquid, 1-ethyl-3-methylimidazolium acetate (EmimOAc), which has both lignocellulose-dissolution and organocatalytic abilities. Efficient homogeneous reactions of bagasse were successfully proceeded under mild conditions without any additional acid catalysts and corrosive reagents, and a successive separation of polysaccharide acetate and lignin acetate was achieved with by taking a difference of solubility in methanol. Acetylation ratio of the polysaccharide acetate and lignin acetate obtained at 80ºC for 30 min were 83% and 71%, respectively. Detail analysis of reaction rates by quantitative ^{31}P NMR method1) revealed that lower reactivity of phenolic OH in lignin than alcoholic OH in the case of transesterification using the EmimOAc catalyst.

Keywords: Lignocellulose, Organocatalyst, Acetylation, Chemical modification, Homogeneous reaction

2017-206

テトラブチルアンモニウムヒドロキシドを反応媒体としたリグニンの化学変換

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Lignin Conversion with Tetrabutylammonium Hydroxide as a Reaction Medium

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Abstract: Aerobic oxidation of various types of lignin in tetrabutylammonium hydroxide (TBAH) produces vanillin and its related phenols with high selectivity. This study addresses degradation of Japanese cedar (*Cryptomeria japonica*) wood flour in a 1.25 M TBAH solution with the O_2 and OH^- concentrations being enhanced by introduction of O_2 and NaOH addition to the system. The TBAH treatment of the wood gave vanillin, vanillin acid, and acetoguaiacone with 23.0, 1.2, and 1.9 wt% yields based on the Kason lignin amount, which were comparable to those obtained with the alkaline nitrobenzene (AN) oxidation. Our further investigation with lignin model compounds revealed that β-*O*-4 and β-5 linkages formed vanillin in the TBAH treatment whereas the AN oxidation produced vanillin only from β-*O*-4 linkage. This strongly suggests that mechanisms in the vanillin formation are significantly different between the TBAH treatment and AN oxidation.

Keywords: Vanillin, Quaternary ammonium, Oxidation, Alkali, Mechanism

2017-207

リグニンフェノール性末端の構造解析と酸触媒ソルボリシスにおける反応性：スギとユーカリの比較

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Reactivity of free phenolic end units in lignin during acid-catalyzed solvolysis: comparison of *Cryptomeria japonica* and *Eucalyptus globulus*

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Abstract: Free phenolic groups in lignin were selectively methylated to investigate how the phenolic terminal and non-phenolic units are released via the β-*O*-4 cleavage during the toluene-methanol microwave solvolysis. Thioacidolysis of the methylated woods of *C. japonica* and *E. globulus* showed that the relative proportions of the G units derived from the phenolic end units are higher than those of S units. The result of the acid-catalyzed toluene-methanol solvolysis of the methylated wood showed that the preferential release of the C6-C2 monomeric degradation products from the phenolic units are observed only in G units, whereas the S monomers were released mainly from the non-phenolic ether-linked units in lignin. The reactivity of the phenolic units during solvolysis was shown to be different between softwood G lignin and hardwood SG lignin.

Keywords: guaiacyl, syringyl, phenolic hydroxyl groups, thioacidolysis, solvolysis.

2017-208

PEG・バイサルファイト法タケ液化物を用いたエレクトロスピニング処理によるカーボンファイバーの調製

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Preparation of carbon fiber by electrospinning using liquefied bamboo from PEG-bisulfite method

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Abstract: Liquefaction of whole bamboo and bamboo-lignin had been successfully performed by PEG-bisulfite method. We tried production of carbon fiber (CF) from liquefied bamboo with cellulose acetate or cellulose triacetate by electrospinning and carbonization treatment. The CF products were analyzed with field emission-type scanning electron microscopy (FE-SEM) and Raman spectrometry. FE-SEM micrographs showed the fibrous structures with average diameters ca. 30 nm from cellulose triacetate and liquefied bamboo-lignin cooked at 200°C for 60 min. As the results of Raman spectrometry, this CF indicated the highest degree of graphite among the other samples. This PEG-bisulfite liquefaction can be used for preparation of the CF from bamboo and bamboo lignin.

Keywords: Bamboo-lignin, PEG-bisulfite method, Carbon fiber, Biorefinery and Electrospinning

2017-209

中山間地域導入型PEG改質リグニン製造システムの開発

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Polyethylene Glycol Lignin Derivatives (Glycol Lignin) Production System for the Operation in a Rural Area of Japan

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Abstract: Acid catalyzed solvolysis of Japanese cedar wood was performed using polyethylene glycol (PEG) as a solvolysis reagent. Since PEG is a high boiling point solvent, the PEG solvolysis reactor can be operated under atmospheric pressure without using pressure equipment. This simple and safe operability brought a concept of introducing a small scale rural area biorefinery system to produce PEG modified lignin derivatives (glycol lignin). Since physical properties of the glycol lignin were very improved, various functional glycol lignin based products such as heat resistant films, activated carbon fiber and FRPs were developed. A bench scale pilot plant was constructed to demonstrate stable glycol lignin production funded by a national research program of Strategic Innovation promotion Program (SIP). In this paper, performance of the pilot scale plant and the characterization of the glycol lignin were discussed.

Keywords: Solvolysis, PEG, Pilot plant, Bio-refinery, Glycol lignin

2017-P01

ゲノム編集技術を用いた抑制型転写因子欠損によるリグニン増強イネの作出

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Molecular-breeding of lignin-enriched rice by knockout of transcription factor genes associated with down-regulation of lignin biosynthesis using a genome editing technique

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Abstract: Large-sized gramineous (Poaceae) plants such as *Sorghum* and *Erianthus* show higher biomass productivity and environment-adaptive capacity than tree species, and have received much attention as sustainable feedstock. On the other hand, the content of lignin, which is a major component of plant cell-walls, is generally lower in gramineous species than in woods. Lignin has a promising market potential as chemicals to produce valuable materials, and could increase the heating value of biomass, because it has much larger heating values than polysacchadides. Therefore, increasing lignin content is a positive strategy to upgrade biomass utilization. In this study, we attempted to increase lignin content of rice (*Oryza sativa*) by knockout of the genes that encode transcription factors (TFs) which act as repressors for the lignin biosynthesis. First, we selected putative repressor-type TFs (MYB and WRKY) lignin biosynthesis in previous reports and obtained their homologous sequences in *Oryza sativa.* Then, using the CRISPR/Cas9 system, targeted mutagenesis in the first exon of each target gene was carried out. We could find several rice lines displaying increased lignin content in generated transformant populations.

Keywords: Lignin, *Oryza sativa*, MYB, WRKY, CRISPR/Cas9 system

2017-P02

β-アリールエーテル代謝中間体のグルタチオン脱離に関与する glutathione *S*-transferase

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Glutathione *S*-transferases involved in the removal of glutathione from intermediate metabolites of arylglycerol-β-aryl ether

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Abstract: *Sphingobium* sp. strain SYK-6 is able to utilize various lignin-derived biaryls including β-aryl ether-type biaryls as the sole source of carbon and energy. In the SYK-6 cells, four stereoisomers of a β-aryl ether-type biaryl, guaiacylglycerol-β-guaiacyl ether are converted into two enantiomers of α-glutathionyl-β-hydroxypropiovanillone (GS-HPV) via stereospecific Cα oxidation and ether cleavage. It was previously thought that (β*R*)-GS-HPV was converted into HPV only by the reaction catalyzed by a glutathione *S*-transferase (GST), LigG. However, the GST genes actually involved in the conversion of both GS-HPV enantiomers in SYK-6 had not yet been identified. In this study, we identified and characterized the GST genes responsible for the conversion of GS-HPV enantiomers. Four GST genes found in SYK-6 were expressed in *E. coli*, and the ability of the gene products to convert both (β*R*)-GS-HPV and (β*S*)-GS-HPV was examined. As a result, the gene products of *ligG* and *ligQ* converted both enantiomers into HPV. Characterization of SYK-6 mutants of *ligG* and *ligQ* showed that both genes were not only involved in the conversion of (β*R*)-GS-HPV and (β*S*)-GS-HPV, but also played major roles in their conversion.

Keywords: bacteria, β-*O*-4 linkage, glutathione *S*-transferase biodegradation

2017-P03

Streptomyces sp. SirexAA-E 株由来のジオキシゲナーゼを発現する組換えポプラの解析

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Analysis of transgenic hybrid aspen harboring dioxygenase derived from *Streptmyces* sp. Strain SirexAA-E

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Abstract: Plant biomass is focused as carbon neutral resources in today, when it is concerned of depletion of fossil fuel. Woody biomass is account for large percentage of plant biomass focused as ingredient of biofuels and biomaterials. Secondary cell wall of plants is main part of woody biomass, which is composed of cellulose, hemicellulose and lignin. Cellulose and hemicellulose are easily converted to biofuels and biomaterials. Whereas, lignin is complex polymer and cross-links with cellulose and hemicellulose. Accordingly, efficient removal of lignin is needed for effective utilization of woody biomass as raw materials for fuels and chemicals. By the use of genetic engineering, we try to generate the novel biomass with the lignin which is easy to remove. In this study, we analyzed the transgenic hybrid aspen harboring a gene for a ring cleavage dioxygenase (RCD) derived from *Streptmyces* sp. strain SirexAA-E change in lignin content and its molecular structure.

Keywords: Hybrid aspen, Genetic engineering, Strain SirexAA-E, Dioxygenase, Lignin

2017-P04

ゲノム編集技術を用いたコニフェルアルデヒド 5-ヒドロキシラーゼ及び *p*-クマロイルエステル 3-ヒドロキシラーゼ機能欠損イネの作出と性状解析

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Characterization of loss-of function mutants of rice *CONIFERALDEHYDE 5-HYDROXYLASE* and *p-COUMAROYL ESTER* 3-*HYDROXYLASE* genes
generated using genome-editing system

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Abstract: Aromatic composition of lignin greatly affects usability of lignocellulosic biomass and therefore has been one of the primary targets of cell wall engineering studies. We previously demonstrated that regulations of rice genes encoding CAld5H (OsCAld5H1) and C3′H (OsC3H1) are effective to modulate lignin aromatic composition in rice. Here, we generated *OsCAld5H1*- and *OsC3H1*-deficient knock-out mutants using the CRISPR/Cas9-mediated targeted mutagenesis. We obtained various rice T_0 lines with small deletions or insertions in the targeted *OsCAld5H1* and *OsC3H1* genomic regions that result frame shift or truncation of the proteins. We then isolated T_1 plants with high mutation efficiency and subjected their mature cell wall tissues for a series of structural analyses using chemical and NMR spectroscopic methods.

Keywords: lignin, *Oryza sativa*, coniferaldehyde 5-hydroxylase, *p*-coumaroyl ester 3-hydroxylase, CRISPR/Cas9 system

2017-P05

(*Z*)-ヒノキレジノール合成酵素 β サブユニットの X 線結晶構造解析

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X-ray crystallographic analysis of (*Z*)-hinokiresinol synthase β subunit

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Abstract: Hinokiresinols, ones of norlignans with the simplest structure, have (*Z*)- and (*E*)- isomers1). Both (*Z*)- and (*E*)-hinokiresinols are formed from *p*-coumaryl *p*-coumarate enzymatically without any cofactors2, 3). Previously, (*Z*)-hinokiresinol synthase, produced in *Asparagus officinalis*, was suggested to be composed of two distinct subunits, HRSα and HRSβ. Interestingly, recombinant HRSα or HRSβ can catalyze the formation of (*E*)-hinokiresinol while the mixture of both recombinant subunits produces (*Z*)-hinokiresinol with >99% (+)-enantiomer excess4). To clarify this unique molecular mechanisms, elucidation of the structures of two subunits with X-ray crystallographic analysis is essential. In this study, the crystal structure of HRSβ was solved, and suggested that HRSβ formed a dimeric structure in the crystals. Furthermore, the crystal structure of HRSβ in complex with a ligand showed the probable location of the active site in HRSβ.

Keywords: norlignan, *Asparagus officinalis*, hinokiresinol, (*E*)-hinokiresinol synthase, X-ray crystallography

2017-P06

形態観察と遺伝子発現解析によるクサトベラの果実二型の比較

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Comparative analyses of morphology and transcriptome between dimorphic fruits of *Scaevola taccada*

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Abstruct: *Scaevola taccada* (Asterales: Goodeniaceae) is a common coastal shrub throughout subtropical and tropical regions. Fruit dimorphism (genetically determined two types of fruit morphology), i.e., cork- and pulp-morphs, has been reported, and the mesocarp of fruit tissue is lignified in the former morph (Emura et al. 2014). The two morphs differ in seed dispersal ability and habitat preference (Emura et al. 2014). To understand the morphological difference and genetic basis, we conducted the following comparative studies. We compared fruit anatomy and lignin deposition between the morphs using optical and ultraviolet microscopy. Gene expressions in fruit tissues were investigated by RNA-seq, and we found distinctive expression levels in the series of lignin-synthesis genes between the two morphs.

Keywords: fruit, morphology, RNA-seq

2017-P07

シロイヌナズナにおけるリグニン構造改変遺伝子の探索

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Search for lignin structure modified genes in *Arabidopsis thaliana*

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Abstract: Plant cell wall, especially lignocellulose enriched in secondary cell wall, provides physical rigidity for plant normal growth and also has a large potential as a resource to produce next-generation biofuel and biomaterials. However, its recalcitrance hampers the industrial use and therefore, the development of innovative technology to improve it is desired. This proof-of-concept study established the screening method for identification of lignin modification enzyme genes under the control of the *poplar C4H* promoter, which functioned in the lignified cells and tissues in *Arabidopsis thaliana*. Some resultant transgenic plants showed the change of lignin staining with phloroglucinol-HCl and/or $KnMO_4$-HCl and high glucose productivity from cell wall residue by cellulase. These results indicated that this approach is powerful tool to identify the gene which improves cell wall quality by modifying lignin structure.

Keywords: *Arabidopsis thaliana*, lignin modification, C4H promoter, glucose productivity

2017-P08

酸化銀によるシナピル *p*-クマレートの酸化カップリング

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Oxidative Coupling of Sinapyl *p*-Coumarate by Using Ag_2O

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Abstract: Among the interunit linkages in lignin, a β-*O*-4 bond is one of the most important bonds. The frequency of the β-*O*-4 bond is about 50-60% in wood lignins. In contrast, it is reported that the frequency reaches more than 80% in some herbaceous plant such as kenaf and abaca. The γ-position of these lignins are highly acylated with acetic acid and *p*-coumaric acid. It is thought that the γ-acylated monolignols may couple to form the β-*O*-4 bond more frequently than non-acylated monolignols. In this study, the oxidative coupling of sinapyl *p*-coumarate was carried out with Ag_2O to better understand the high frequency of the β-*O*-4 bond in acylated lignins.

Keywords: sinapyl alcohol, monolignol, β-ether, silver oxide, HMBC NMR

2017-P09

リグニン形成初期におけるモノリグノール二量体の脱水素重合

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Dehydrogenation polymerization of monolignol dimer in the first of forming lignin

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Abstract: It is believed that polymerization of lignin proceeds by continuous coupling of free radicals of monolignol which is the precursor of lignin. Many studies have investigated biosynthesis of monolignol, but it is still unclear. In our previous study, the polymerization of monolignol dimers using horseradish peroxidase (HRP) was investigated, because HRP is available and the one of the most accessible enzymes. However, it is unclear whether HRP can apply to lignin formation in actual trees. In this study, we exracted enzymes from *Chamaecyparis obtusa* , and carried out enzymatic dehydrogenation polymerization with the extracted enzymes. The results obtained were compared with that of the previous study using HRP, and biosynthetic process of lignin inside the actual tree was investigated.

Keyword: dilignol, dehydrogenation polymerization, Chamaecyparis obtuse, erythro/threo, radical coupling

2017-P10

原子間力顕微鏡による単離リグニン孤立分子の直接観察

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Observation of isolated lignin single molecule by atomic force microscopy

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Abstract: Lignin is a natural polymeric compound with complicated and random structures. Many studies have elucidated the structures of lignin by means of chemical analysis and NMR, while these are the average ones. Microscopic and direct visualization of the molecular structure of lignin is a challenging task. In this study, we explore polymers miscible with isolated lignin and subject the blend system to atomic force microscopy (AFM) in order to observe the lignin structure. Visualization of molecular shape of macroscopic lignin will give us new insights into the structural studies of lignin.

Key word: blend, single molecule, visualization, DSC,

2017-P11

アルカリ性下におけるリグニンのキノンメチド構造生成に及ぼす芳香核構造および側鎖構造の影響

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Effect of the type of aromatic nucleus and side-chain structure on the formation of quinone methide structure in lignin under alkaline conditions

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Abstract: Although quinone methide (QM) is an important intermediate in various reactions of lignin, the formation and reactions of QM have not yet been examined well. The purpose of this study is to examine the effect of the type of aromatic nucleus and side-chain structure on the formation of QM, employing simple lignin model compounds. Regarding the type of the aromatic nuclei, the formation rate of QM was in the order of the model compounds consisting of: syringyl nucleus > guaiacyl nucleus > *p*-hydroxyphenyl nucleus. This result suggests that the methoxy group(s) located at the *meta*- of the benzyl carbon promotes the formation of QM. This tendency was exactly the reverse of the formation rate of the benzyl cation structure (a conjugate base of OM) under acidic conditions. Regarding the influence of the side chain structure, it was suggested that the model compound with the secondary benzyl carbon is more favorable for the formation of QM than those with the primary benzyl carbons.

Keywords: inductive effect, electron withdrawing, conjugation, alkene

2017-P12

Sphingobium sp. SYK-6 株における 5-5’型リグニン二量体化合物代謝系遺伝子の転写制御機構

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Transcriptional regulation of the catabolic genes of a 5-5’-type lignin-derived biaryl compound in *Sphingobium* sp. strain SYK-6

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Abstract: *Sphingobium* sp. SYK-6 degrades various lignin-derived biaryls and monoaryls. A 5-5’-type lignin-derived biaryl compound, 5,5’-dehydrodivanillate (DDVA), is catabolized by SYK-6 via vanillate after O demethylation, aromatic ring cleavage, side chain cleavage, and decarboxylation. In the DDVA catabolic genes of SYK-6, the transporter genes (*tbtA* and *ddvK*) and the catabolic enzyme genes (*ligZ*, *ligY*, and *ligXa*) form a gene cluster. The *ddvR* gene which encodes a MarR-type transcriptional regulator is located in this cluster. The objective of this study was to elucidate the transcriptional regulation of the DDVA catabolic genes. Reverse transcription (RT)-PCR analysis showed that the DDVA catabolic gene cluster consists of three operons, including the *ligXa* operon, the *ddvR* operon, and the *tbtA* operon which contains *ddvK*, *ligZ*, and *ligY*. Quantitative RT-PCR analysis using SYK-6 and *ddvR* mutant cells revealed that the transcriptions of the *ligXa* and *tbtA* operons were negatively regulated by DdvR, and DDVA was identified as an inducer. On the other hand, the *ddvR* operon was constitutively expressed.

Keywords: 5-5’ linkage, biphenyl, biodegradation, bacteria, repressor

2017-P13

テトラブチルアンモニウムヒドロキシド中における β-*O*-4 型リグニンモデル化合物の分解挙動

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Degradation of β-*O*-4 Type Lignin Model Compounds in Tetrabutylammonium Hydroxide Solution

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Abstract: In tetrabutylammonium hydroxide (TBAH) lignin is degraded selectively into low molecular weight compounds, especially vanillin. This study addresses degradation of phenolic and non-phenolic β-*O*-4 type lignin model compounds in 1.25 M TBAH and NaOH solutions, focusing on differences in reaction behaviors of the models and several intermediates between TBAH and NaOH. In the phenolic model, vanillin was produced via aerobic oxidation of an enol ether intermediate. The Bu_4N^+ cation stabilized the intermediate, resulting in suppressed formation of vanillin from the phenolic model in TBAH. The non-phenolic model gave veratraldehyde (precursor of vanillin) though two steps: β-ether cleavage of the model to veratryl glycerol intermediate, followed by the aerobic oxidation of the glycerol side chain. In TBAH, both steps were greatly enhanced, so that the model gave vanillin in much higher yield in TBAH than in NaOH.

Keywords: degradation, vanillin, tetrabutylammonium hydroxide, model compound, alkali

2017-P14

水熱処理による種々リグノセルロースのリグニン分解挙動

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Decomposition behaviors of lignin in lignocellulosics by hydrothermal treatment

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Abstract: The decomposition behaviors of lignin in various lignocellulosics as treated by hot-compressed water (230°C/10 MPa/15 min) were compared. As a result, the delignification from monocotyledons such as nipa (*Nypa fruticans*) frond, rice (*Oryza sativa*) straw and corn (*Zea mays*) cob was more extensive than that from woods such as Japanese cedar (*Cryptomeria japonca*) and Japanese beech (*Fagus crenata*). From GPC analysis, it was found that lignin in water-soluble portion from monocotyledons was relatively higher in its molecular weight compared to that from woods. In the water-soluble portion from monocotyledons, phenolic acids were retrieved with a high yield.

Keywords: Cinnamic acids; Delignification; Hydrothermal treatment; Lignin; Lignocellullosics

2017-P15

テトラブチルアンモニウムイオン存在下におけるスギリグニンの酸素による低分子化

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Aerobic Oxidation of Japanese Cedar Lignin in the Presence of Tetrabutylammonium Ion

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Abstract: Aerobic oxidation of lignin in tetrabuthylammonium hydroxide (TBAH) solution gives vanillin and vanillic acid with high selectivity. This study presents TBAH degradation of Japanese cedar (*Cryptomeria japonica*) under O_2 compressed at 1.0 MPa. The TBAH degradation with the addition of NaOH under the compressed O_2 gave vanillin and vanillic acid with 8.6 and 1.5 wt% yields, which were significantly improved from those obtained under non-compressed O_2. The compressed oxygen was also effective for reduction of required reaction temperature and time.

Keywords
Vanillin, Quaternary ammonium, Oxidation, Alkali, Compressed O_2

2017-P16

金属塩を用いたリグニンの新規中性加水分解システムの構築

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Establishment of a novel neutral hydrolysis system for lignin using metal salts

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Abstract: A neutral H_2O solution containing LiCl, LiBr, LiI, NaCl, NaBr, NaI, KCl, KBr, or KI was employed to examine whether or not the cations and/or anions consisting of these salts can induce a reaction of the *erythro* isomer of veratrylglycerol-*β*-guaiacyl ether (VG-*E*) at 160℃. The pH of most solutions was not exactly neutral, which would affect the obtained results. The isomerization to the *threo* isomer was observed in all the solutions except the LiI solution, where the pH was slightly alkaline (≈10). In the LiI solution, reactions other than the isomerization occurred most significantly. Veratraldehyde was detected as the only major degradation product.

Keywords: Alkyl-aryl ether, *β*-*O*-4 bond, Pulp, Wood

2017-P17

酸加溶媒分解スギリグニン中の糖由来変性物の解析

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Characterization of denatured carbohydrate in the polyethylene glycol solvolysis lignin prepared from Japanese cedar

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Abstract: The process of acid-catalyzed PEG solvolysis of Japanese cedar to produce PEG-lignin has being developed at FFPRI in order to promote an effective utilization of woody biomass. Because of the introduction of PEG onto lignin side-chains, the PEG-lignin possess thermal fusible property. In our previous study, some furan structural pyrolysis compounds were detected in PEG-lignin pyrogram, which indicated that PEG-lignin contained a trace amount of furan based polymer. It was suggested that carbohydrate was denatured into furan based polymer. In order to confirm that hypothesis, a model experiment of PEG solvolysis of glucose, xylose, and holocellulose of Japanese cedar was conducted and investigated the generation of denatured carbohydrates by Py-GC/MS. Some furan structural pyrolysis compounds were detected in pyrogram of residues from model samples. The results indicated that the furan based polymer detected in PEG-lignin are generated from carbohydrate components of wood through solvolysis process as denatured carbohydrate.

Keywords: solvolysis, PEG-lignin, Pyrolysis Gas chromatography/Mass spectrometry, carbohydrate, furan based polymer

2017-P18

Phanerochaete sordida YK-624 株が有する Mn トランスポーター遺伝子の機能解析

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Functional analysis of Mn transporter gene possessed by *Phanerochaete sordida* YK-624

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Abstract: A homologue gene of natural resistance-associated macrophage protein (Nramp) family transporter *smf2* was identified in white rot fungus *Phanerochaete sordida* YK-624. Relative expression level of the homologue, named *PsMnt*, were roughly same in the cultures containing 0 to 1000 µM Mn(II), nontoxic concentration to growth of the fungus. In *PsMnt* homologous overexpressed mutant, cellular Mn accumulation and the exhibited manganese peroxidase (MnP) activity were significantly increased in the 4-day culture containing10 µM Mn(II). In comparison of wild type strain, MnP activity of the overexpressed mutants were largely increased in lower Mn concentration (specifically 15-20 times higher at 1µM Mn(II) and 7-8 times at 10 µM). Although there was no difference in MnP activity secreted during beech wood decay between overexpress and control strains, slight but significant higher activity was observed in overexpressed strain on cedar wood meal medium than control. From these results, it was suggested that the *PsMnt* is a high-affinity Mn transporter involved in cellular Mn accumulation in Mn deficient condition. This is the first report about *smf2* homologue in wood rot fungi.

Keywords: *Phanerochaete sordida* YK-624; Mn transporter; Manganese peroxidase

2017-P19

アルカリ系蒸解により分離されたリグニンの低分子化－ 硫酸-過酸化水素処理と再生二酸化マンガン処理－

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Depolymerization of lignin isolated from alkali-AQ cooking liquor - H_2O_2 /H_2SO_4 treatment and *in situ* generated MnO_2 treatment-

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Abstract: The lignin obtained from the alkali-AQ cooking liquor was subjected to H_2O_2 /H_2SO_4 treatment or manganese dioxide treatment to reduce the molecular weight. Although the polymerization of lignin was observed to occur by acid treatment, the molecular weight of the treated lignin became smaller with the increase of the hydrogen peroxide concentration during the H_2O_2 /H_2SO_4 treatment. Within the treatment condition examined, the longer reaction time and higher reaction temperature resulted in the lower molecular weight under the same hydrogen peroxide concentration. In case of MnO_2 treatment, because the solubility in THF of the acetylated derivative of the treated lignin was low, the amount of MnO_2 treated lignin detected by GPC was only half of the original lignin. The molecular weight of this detected part of the MnO_2-treated lignin was clearly lower than that of untreated lignin.

Keywords: Sugi lignin, Alkali-AQ cooking, H_2O_2 /H_2SO_4 treatment, MnO_2 treatment, GPC

2017-P20

タンデムダイマー化したリグニン親和性ペプチドの結合解析とペプチド配列を担持した酵素によるリグニン分解

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Binding analysis of tandem dimer of lignin-binding peptide and lignin degradation by the peptide-bearing enzyme

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Abstract: For the establishment of lignocellulose biorefinery system through production of biofuels and aromatic chemicals from lignocellulosic biomass, highly selective lignin degradation is required. We recently discovered a lignin-binding 12-mer peptide by the phage display technique. The peptide is a potential novel tool improving affinity of (bio)catalysts to the substrate lignin. In this study, we improved the affinity of the peptide to lignin by 10 times through tandem dimerization of the two lignin-binding peptide sequences. The tandem dimer peptide changed its conformation on addition of lignin to recognize the structural differences in the lignin from softwood and hardwood. In addition, we comparatively analyzed the properties of oxidative enzyme bearing the tandem dimer peptide.

Keywords: Lignin binding peptide, FTIR, conformation change, lignin degrading enzyme

2017-P21

ヒト腸内細菌 *Blautia producta* ATCC27340 におけるリグナン *O*-デメチラーゼの探索

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Search of a lignan *O*-demethylase from a human intestinal bacterium, *Blautia producta* ATCC27340

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Abstract: A lignan glycoside, secoisolariciresinol diglucoside (SDG), is one of the most abundant dietary lignans. After oral administration of SDG, SDG is converted into the mammalian lignans, enterodiol (ED) and enterolactone (EL), by human intestinal bacteria. The mammalian lignans are lignan-type phytoestrogens and contribute the reduction of risk of breast cancer in females. Elucidation of the formation mechanism for mammalian lignans could be useful for further reduction of risk of breast cancer. In addition, the *O*-demethylation and dehydoxylation of aromatic rings in mammalian lignan formation attract a great attention because these reactions are essential for eliminating methoxyl substitutions in aromatic monomers or oligomers derived from depolymerized lignin in lignin biorefineries. To date, few human intestinal bacterial species including *Eubacterium limosum* and *Blautia producta*, have been known to catalyze *O*-demethylation, and very recently a tetrahydrofolate-dependent secoisolariciresinol (SIR) *O*-demethylase has been identified in *E. limosum* ZL-II. Thus far, however, any *O*-demethylase has not been identified in other bacteria. To get more information of *O*-demethylation mechanisms in mammalian lignan biosynthesis, we aim at identifying a lignan *O*-demethylase in *B. producta* ATCC27340.

Keywords: tetrahydrofolate-dependent *O*-demethylase, mammalian lignan, human intestinal bacteria, *Blautia producta*, anaerobic condition

2017-P22

Sphingombium sp. YG1 由来 guaiacylglycerol-β-guaiacyl ether - Cα 位酸化酵素の酵素学的解析と利用

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Enzymatic characterization and application of guaiacylglycerol-β-guaiacyl ether – Cα-dehydrogenases from *Sphingobium* sp. YG1

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Abstract: A bacterial enzymatic cascade for β-*O*-4 reductive cleavage in lignin model dimers consists of Cα-dehydrogenases belonging to short-chain dehydrogenase/reductase (SDR) superfamily, β-etherases and β-glutathione thioetherases (glutathione lyases) belonging to glutathione-S-transferase (GST) superfamily. In this study, enzymatic characterization of a recently identified Cα-dehydrogenase from *Sphingobium* sp. YG1 isolated from Kagoshima Bay was conducted. The recombinantly-expressed enzyme showed higher activity for hydroxyl moiety at Cα (benzyl) position of guaiacylglycerol-β-guaiacyl ether (GGGE) than the other reported homologous enzymes. The enzyme could act on a lignin fraction extracted from hard wood (*Eucalyptus globulus*), indicating future applications as a tool for lignin enzymatic conversion.

Keywords; β-*O*-4 linkage, enzymatic cleavage, Cα-dehydrogenase, short-chain dehydrogenase/reductase, *Sphingobium*

2017-P23

フラグメント分子軌道法を活用したリグニン β-O-4 還元開裂酵素の機能改変

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Analysis of β-*O*-4 cleaving enzyme, GST4, from the marine bacterium, *Novosphingobium* sp. MBES04

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Abstract

The marine bacterium, *Novosphingobium* sp. MBES04, isolated from a sunken wood was capable of metabolizing the stereoisomers of β-*O*-4 lignin dimers into the respective monomers (phenylpropane units) by combination of five enzymes. A GST4 is a glutathione-dependent β-etherase, and one of the key enzymes in the pathway which selectively catalyzes reductive cleavage of β-*O*-4 aryl-ether bonds in lignin. In this study, we tried to improve the activity of GST4 by computational assisted molecular designing using the fragment molecular orbital (FMO) method so that the enzyme can convert lignin more efficiently. Mutational studies demonstrated that single or double amino acid substitution mutants, GLY117ALA and HIS39GLN_GLY117ASP showed considerable improvement in their specific activities.

Keywords: Lignin, *Novosphingobium*, GST, fragment molecular orbital method, FMO

2017-P24

リグニンの *t*-ブチル化による自己縮合反応制御

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t-Butylation of lignin for preventing the self-condensation

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Abstract: Hinoki wood meal was treated with concentrated sulfuric acid prepared with *t*-butyl alcohol and

95 % sulfuric acid to prevent self-condensation reaction of lignin. The reaction mixture was diluted, boiled and the acid insoluble fraction was recovered. The yield of the acid insoluble fraction was higher than that simply treated with 72 % sulfuric acid and the FT-IR spectrum demonstrated remarkable absorption of methyl groups. The solubility of the acid insoluble fraction in various organic solvents was significantly increased by addition of *t*-butyl alcohol. TMA curves showed that it has thermal fluidity. These results suggest that the self-condensation of lignin was successfully prevented by *t*-butylation of the lignin.

Keywords: *t*-butyl alcohol, concentrated sulfuric acid, self-condensation, solubility, fluidity

2017-P25

改質リグニン製造システムへの薬液再生プロセスの導入

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Development of solvent regeneration process in the PEG solvolysis system for glycol lignin production

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Abstract: The acid-catalyzed solvolysis system of Japanese cedar using a glycol solvent is being developed to produce glycol modified lignin derivatives (glycol lignin). To decrease operational costs, a glycol solvent used as a solvolysis liquor need to be recovered and reused. In this study, the solvolysis liquor, polyethylene glycol (PEG), was recovered by removal of water from the supernatant of solvolysis liquor after glycol lignin precipitation, and the recovered PEG was reused in next production line. A diluted acid hydrolysis treatment was conducted to the recovered PEG in order to activate the reactivity of the PEG. The amount of the terminal hydroxyl groups of the recovered PEG was increased by the hydrolysis treatment. The reactivity came back to the level of fresh PEG by the regeneration process of the hydrolysis.

Keywords: Acid-catalyzed solvolysis; Glycol lignin; Polyethylene glycol (PEG); Solvent regeneration; Softwood

2017-P26

テトラブチルアンモニウムヒドロキシドを用いたバニリン生産における生成物の分離精製法の開発

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Separation of Vanillin from the Reaction Mixture Formed in Degradation of Lignin in Tetrabuthylammonium Hydroxide solution

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Abstract: Aerobic oxidation tetrabutylammonium hydroxide (TBAH) gives vanillin with high selectivity. For industrial application of the TBAH method, development of vanillin isolation techniques is indispensable. To this end, this study addresses extraction of vanillin from the alkaline solution obtained after the TBAH treatment of Japanese cedar (*Cryptomeria japonica*) by EtOAc. Our investigation clarified that vanillin was efficiently extracted with EtOAc regardless of the acidification process by HCl aq. before the extraction. The direct extraction of vanillin from the alkaline solution was feasible probably because of decrease in pH of the solution by the AcOH formation from EtOAc by OH- and the ion pair formation between the vanillin anion and the Bu_4N^+ cation.

Keywords: vanillin isolation, extraction, alkaline solution, EtOAc, ion pair formation

2017-P27

テトラブチルアンモニウムヒドロキシド中における β-5 型構造からのバニリン生成

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Vanillin Production from a β-5 Type Lignin Model Compound in Tetrabutylammonium Hydroxide-$30H_2O$

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Abstract: Degradation of lignin in the presence of tetrabutylammonium hydroxide (TBAH) and oxygen gives vanillin and its related compounds with high selectivity. This study presents degradation behavior of β-5 type and β-*O*-4 type lignin model compounds in their TBAH treatment and alkaline nitrobenzene (AN) oxidation. In the TBAH treatment vanillin was produced both from the β-5 and β-*O*-4 models with moderate yields of 59.9 and 40.3 mol%, respectively. In the AN oxidation, although the β-*O*-4 model gave vanillin with very high yield of 91.2 mol%, the β-5 model did not yield vanillin, at all. These results suggest that lignin polymers produce vanillin from β-5 and β-*O*-4 structures in the TBAH treatment, whereas only β-*O*-4 structures are subjected to vanillin formation in the AN oxidation.

Keywords: vanillin, β-5 linkage, model compound, alkaline nitrobenzene oxidation, tetrabutylammmonium hydroxide,

2017-P28

イオン液体中でのマイクロ波照射によるスギ木粉からのメチルグリコシドの合成

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Synthesis of methyl glycoside from Japanese cedar (*Cryptomeria japonica*) in ionic liquid under microwave irradiation

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Abstract: Conversion of a lignocellulosic biomass into useful substances has attracted increasing attention in recent years. In this study, acid-catalysed conversion of cellulose to methyl glucoside was investigated by using microwave reactor and ionic liquid as a solvent. Microcrystalline cellulose (Avicel) was reacted with acetyl chloride (AcCl)-MeOH in 1-allyl-3-methylimidazolium chloride ([Amim]Cl)/*N*-methyl-2-pyrrolidone (NMP). By oil bath heating, methyl α, β-D-glucopyranoside was generated in 43% yield. In contrast, MW heating resulted in 71% yield. The yield decreased to only 6% by MW heating when MeOH was used as a solvent instead of [Amim]Cl/NMP treatment. The results showed that the combined use of MW heating and ionic liquid effectively improved the conversion of Avicel to methyl glucopyranoside. Conversion of Japanese cedar into methyl glycoside was also conducted under the same conditions.

Keywords: biorefinery, ball-milled wood, acid-catalyst, microwave, ionic liquid

2017-P29

Effect of starting wood meal type on properties of glycol lignin produced by acid-catalyzed polyethylene glycol (PEG) solvolysis

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Abstract: In this work, three types of sugi wood meal were used as starting material to isolate PEG-substituted lignin, namely glycol lignin (GL) by acid-catalyzed polyethylene glycol (PEG) solvolysis process. The effect of sugi wood meal type, especially the meal size on the properties of lignin products, such as lignin contents, molecular weight, structural and thermal behavior were then investigated.

Keywords: glycol lignin, polyethylene glycol (PEG) solvolysis, wood meal size, 2D NMR, TMA

2017-SP1

細胞壁の木化

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Lignification of cell wall

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Abstract: Lignification starts at cell corner middle lamella when the secondary wall formation starts, and then proceeds toward compound middle lamella. Lignification of secondary wall starts at cell corner region of outer S1 layer, proceeds toward outer S1 layer, and then centripetally lagging behind cell wall thickening. Monolignols are synthesized by the catalytic reactions of enzymes localized in the cyto-sol and on the membrane of cell organelle during secondary wall formation. They are transported toward the cell wall by some mechanism, and polymerized to form globular structures of lignin.

Keywords: lignification, lignin, middle lamella, monolignol, secondary wall

2017-SP2

木部道管二次細胞壁のリグニン沈着の制御メカニズム

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Regulatory mechanisms underlying lignin deposition on secondary cell walls of xylem vessels

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Abstract: We previously established the in vitro systems for vessel cell differentiation, which include lignification of secondary cell walls (SCWs). The transcriptome analyses with the culture systems identified a number of genes related to lignification of SCWs and the regulation of vessel cell differentiation. Detailed analysis of these genes revealed the mechanisms of SCW lignification. For example, it was found that lignin deposition in SCWs is not dependent on cellulose patterning. Also, two previously uncharacterized DOF transcription factors are found to have a suppressive function on the lignin deposition in Arabidopsis stem vasculature. We will discuss about such the knowledge on SCW lignification revealed through the in vitro systems.

Keywords: DOF transcription factor; in vitro culture system; secondary cell wall; VNS transcription factor; xylem vessel

2017-SP3

陸上植物の進化と木化のバイオメカニックス

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Biomechanics of evolution of wood in terrestrial plant

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Abstract: In this presentation, physical meanings of secondary xylem formation and its development are discussed from the viewpoint of evolutionary strategy of terrestrial plant. We start our discussion from mechanical implication of occurrence of vascular bundle tissue and eustele stem in ancient plant. And our discussion focuses on the growth stress generation as a new technique for surviving the race of forest trees for growing mammoth.

Keywords: plant history, paleobotany, secondary xylem, growth stress, eustele

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2018-101

中性付近におけるハロゲン化アルカリ金属を用いた新規脱リグニン系の検討

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Establishment of a novel delignification system using alkali metal halides under circumneutral pH conditions

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Abstract: A neutral H2O solution containing LiCl, LiBr, LiI, NaCl, NaBr, NaI, KCl, KBr, or KI was treated at 160°C to examine whether or not these salts induce a reaction of veratrylglycerol-β-guaiacyl ether (VG). The pHs of most of these solutions were not exactly neutral, and dependent on the type of the salts. The erythro isomer of VG (VG-e) isomerized to the threo isomer (VG-t) in all the solutions except for the LiI solution, where the pH was relatively higher (≈10) than those in the other solutions. It was confirmed that VG-e isomerizes in the solutions with the pHs lower than 10, which suggests that the benzyl cation generates from VG-e and hence VG-e can possibly undergo the acidolytic reaction route. To quench the possible acidolytic reaction route, the same solutions of VG-t except for those of the K salts were treated after the pHs were arranged to be slightly higher than 10. It was confirmed that the LiI and NaI solutions induce the degradation of VG-t without isomerizing to VG-e (LiI > NaI), which was contrast to the LiCl, LiBr, NaCl, and NaBr solutions. Veratraldehyde and guaiacol were detected as reaction products.

Keywords: Alkyl-aryl ether; β-O-4 bond; Lithium iodide; Sodium iodide

2018-102

Investigation on the Cleavage Reaction of the β-O-4 Bond in Lignin Caused by tert-Butoxide

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Abstract: The erythro or threo isomer of the C6-C3-type non-phenolic β-O-4 lignin model compound, veratrylglycerol-β-guaiacyl ether (IIIe or IIIt, respectively), was reacted in a DMSO solution containing potassium tert-butoxide with a concentration of 0.5 mol/L at 30°C. These reaction conditions were much milder than those employed in a common alkaline pulping process. The results were compared with those obtained in our previous study where the corresponding C6-C2-type compound, veratrylglycol-β-guaiacyl ether (II), was treated under the identical conditions.

The disappearance rates were in the order of: compound IIIe >> compound IIIt > compound II, which is not accordance with those observed in a common alkaline pulping process using NaOH under elevated temperature (compound IIIe > compound II > compound IIIt). This result suggests that the γ-hydroxy group participates in the disappearance reaction of compound IIIe as well as compound IIIt. Because guaiacol (2-methoxyphenol) was not quantitatively liberated accompanying the disappearance of compound IIIe or IIIt in contrast to the reaction of compound II, not only the β-O-4 bond cleavage but also some other reactions contribute to the disappearance of compound IIIe or IIIt.

Keywords: potassium tert-butoxide, non-phenolic, γ-hydroxymethyl group, β-O-4 bond, cleavage.

2018-103

ソーダ蒸解過程における C6-C1 型リグニンモデル化合物の縮合反応に関する定量的研究

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Quantitative Study on Condensation Reaction of C6-C1 type Lignin Model Compounds under Soda Cooking Process

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Abstract: Condensation reaction of lignin was quantitatively examined under common soda cooking conditions using simple C6-C1-type lignin model compounds, vanillyl alcohol (A) and creosol (B). A condensation product was isolated and identified by several NMR analyses to be dimer AB consisting of the α-5-type interunit linkage. The yield of dimer AB was 10% or 50% based on the initial mole amount of compound A, when the ratio of the initial concentrations of compounds A and B was 1/1 or 1/5, respectively.

Chromatographic analyses suggested the formation of the other condensation product, which is not fully identified yet but was also detected in the reaction using only compound A, which indicates that compound A undergoes the self-condensation. Interestingly, in the reaction using only compound A, vanillin (C) and compound B were detected. Although their yields were not very high, the formation of these compounds suggests that the quinone methide primarily derived from compound A can oxidize compound A to generate two compounds: compound B as the reduction product of quinone methide, and, compound C as the oxidation product of compound A. Such a redox reaction of quinone methide may play a certain role in the alkaline delignification process.

Keywords: soda cooking, quinone methide, condensation reaction

2018-104

天然系メディエーターによるリグニン電解酸化の検討

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Lignin oxidation by electrolytic mediator system with natural mediators

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Abstract: It is well-known that lignin degradation products (phenolic compounds with low molecular weight) participate to the lignin microbial degradation as mediators in nature. Therefore, the lignin degradation products are also promising candidates for the mediators in lignin degradation by electrolytic mediator system (EMS). In this study, guaiacyl-type artificial lignin (G-DHP) oxidation by EMS with methyl syringate (MS), acetosyringone (AS), syringaldehyde (SA) as natural mediators were investigated. It was found that the natural mediators showed higher lignin oxidation abilities than the artificial mediators which we have investigated such as NHPI, ABTS and so on, and that C□ -oxidation of G-DHP proceeded preferentially.

Keywords: DHP, Electro-oxidation, EMS, Lignin, Mediator

2018-105

Analysis of microwave effects cleaving covalent bonds of lignin substructures by copper oxide-peroxide reaction

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Abstract: Microwave irradiation promoted production of vanillin and vanillic acid from woody biomass by the reaction with CuO and H2O2 under an alkaline medium. In this study we analyzed if microwave directly accelerates degradation of phenolic (erythro) and non-phenolic (erythro) □-O-4 lignin dimer model compounds under the conditions of the same temperature profile, stirring speed and reaction vessel with those of conventional heating using an oil bath. The main reaction products were vanillin, vanillic acid, veratraldehyde, veratric acid, guaiacol and dicarboxylic acids including fumaric acid, maleic acid, malic acid, malonic acid and succinic acid. Profiles of the microwave accelerating effects are reported.

Keywords: copper oxide, microwave, peroxide

2018-106

水素供与体を含む芳香族溶媒中での木材リグニンの熱分解

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Pyrolytic degradation of lignin in wood in the presence of hydrogen donor and aromatic solvent

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Abstract: Hydrogen donor and aromatic solvent are expected to stabilize lignin primary pyrolysis products against secondary polymerization during lignin pyrolysis by inhibiting the radical coupling and condensation via quinone methide (QM) intermediate, respectively. In this study, cedar wood was pyrolyzed in the presence of

1,2,3,10b-tretrahydrofluoranthene (H-donor) and 1,3-diphenoxybenzene (DPB, aromatic solvent) under the conditions of 350 ℃/N2/5 min. The pyrolysis mixture was extracted with a binary mixture of H2O/EtOAc, followed by the extraction of the EtOAc-soluble portion with n-hexane after evaporation. This procedure was found to be effective for separation of the carbohydrate- (H2O-layer) and lignin-derived (EtOAc-layer-hexane-insoluble) products from the H-donor and solvent, by analyzing these fractions with 1H NMR and GPC. The GC/MS analysis of the hexane-soluble fraction (H-donor and solvent) indicated that the H-donor could be utilized during pyrolysis. With this pyrolysis method, most of the lignin in cedar wood was converted mainly into the oligomers, which were soluble in CHCl3, although the yield was only quite low in the conventional cedar wood pyrolysis. These lignin-derived products can be utilized for further conversion, aiming at the aromatic chemical production.

Keywords: Pyrolysis, aromatic solvent, H-donor, separation, aromatic chemical

2018-107

酵素的脱水素重合における*β*-5 位ジリグノールの挙動解析

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Behavior analysis of β-5 dilignol in enzymatic dehydrogenative polymerization

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Abstract: Lignin is one of the major components of the plant cell wall. The biosynthesis of lignin is started from the formation of dimers by radical coupling of two monolignols. Then, the dimers are subjected to further radical coupling with monolignols or dimers to form oligomaers. In the case of β-5 dimer, it is thought that the phenolic hydroxyl group or 5-position of aromatic ring of ring A were participated in the radical coupling, but there is a possibility that β position of ring B is involved in the reaction.

The purpose of this research is to investigate the reaction of β-5 dimer in the radical coupling. We synthesized the 13C labeled β-5 dimer at the β-position of the ring B (I) through 8-step reactions using vanillin as a starting material. And then we prepared DHPs from I and the unlabeled analogue (II) as a substrate, respectively. The DHPs were analyzed by HSQC NMR. It was observed that the peak intensity was increased at three regions in the HSQC spectrum of DHP made of I by compared with that of II. This results indicated that β-position of the ring B was participated in the radical coupling reactions.

Keywords:β-5 dimer, DHP, HSQC NMR, selective 13C-enrichment

2018-108

SEC-MALLS を用いたクラフトリグニンおよび関連化合物の分子量測定

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Molar mass measurement of kraft lignins and their related compounds with SEC-MALLS

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Abstract: Molar masses of acetylated softwood and hardwood kraft lignins and linear polymeric lignin models, which consisted only of β-O-4 interunitary linkage, were measured on a size-exclusion chromatography equipped with multi-angle laser light scattering detector at 785 nm of incident laser wavelength. Both acetylated kraft lignins indicated much larger (more than 5 times) molar mass than authentic polystyrene standards at any retention time. However, polymeric lignin models showed similar molar masses to the polystyrene standards. This difference in molar mass between acetylated kraft lignins and acetylated lignin models must be attributed to the branched structure of kraft lignins.

Keywords: Absolute molar mass, Mark-Houwink-Sakurada equation, Intrinsic viscosity, Hydrodynamic radius, Self-fluorescence

2018-109

Assembly of electric double layer capacitor with electrode made from lignin and ionic liquid as an electrolyte

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Abstract: Our research group has already reported preparation of electrode material for electric double layer

capacitor (EDLC) from several isolated lignins through electrospinning, carbonization and steam activation. Such EDLC was assembled with lignin-based electrode and organic electrolyte, triethylmethylammonium tetrafluoroborate/propylene carbonate solution (TEMABF4/PC). In this study, to improve an energy density of EDLC, an ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF4), was attempted to be used as the electrolyte, which could expand the operation voltage window due to its electric stability at higher voltage. However, the ionic liquid was larger in molecular size than the organic electrolyte. Therefore, a main objective of this study was to develop lignin-based electrode material with suitable pores for the size of EMIBF4.

A target electrode was obtained from a polymer blend of hardwood kraft lignin (HKL) and polyethylene glycol (PEG) at different ratios as starting materials, which was electrospun followed by thermostabilization, carbonization and steam activation. When PEG ratio was increased to 5%, the resultant carbonaceous electrode had larger BET specific surface area and average pore size compared to those of the electrode prepared with 1% PEG blend. As a result, EDLC with the electrode from 5% PEG blend showed 65 Wh/kg of energy density, which is 1.5–fold that of the EDLC we reported previously.

Keywords: Electric double-layer capacitor (EDLC), Hardwood kraft lignin, Hexamine, Ionic liquid Electrolyte

2018-110

中山間地域導入型PEG改質リグニン製造システムの生産性

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Productivity of the Japan Rural Area Type of the PEG Lignin Derivative (Glycol Lignin) Production System

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Abstract: Acid catalyzed solvolysis of Japanese cedar wood was performed using polyethylene glycol (PEG) as a solvolysis reagent. A bench scale pilot plant was constructed to demonstrate stable PEG modified lignin derivatives (glycol lignin) production funded by a national research program of Strategic Innovation promotion Program (SIP). In this paper, performance of the pilot scale plant was discussed. The total process efficiency analysis showed that the solid-liquid separation process of glycol lignin preparation was the most electric energy consuming process. To improve the efficiency of the filtration, flocculation of the glycol lignin particle was promoted by a heating treatment of the glycol lignin suspension. As the total result, the amount of electricity consumption was reduced to a one-third in the solid-liquid separation process of glycol lignin preparation.

Keywords: Solvolysis, PEG, Bio-refinery, Glycol lignin, Japanese cedar

2018-111

テトテトラブチルアンモニウムヒドロキシドを反応媒体とした各種リグニン試料からのバニリン生産

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Vanillin Production from Several Lignin Samples with Tetrabutylammonium Hydroxide as a Reaction Medium

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Abstract: Aerobic oxidation of lignin in tetrabutylammonium hydroxide (TBAH) produces vanillin and its related phenols with high selectivity. This study addresses vanillin production from several types of lignin such as PEG-modified glycol lignin from Japanese cedar (Cryptomeria japonica) and sodium lignosulfonate in a TBAH-based reaction solution, as compared with the results previously reported for natural lignin in Japanese cedar. The aerobic oxidation (120 oC/air) of the PEG-modified glycol lignin and sodium lignosulfonate (14 mg) as well as the cedar wood in the TBAH-based solution (2.0 mL) resulted in significantly higher vanillin yield than those in a simple alkaline (NaOH) solution, regardless of the presence of the □-sulfo group. We also performed vanillin production from the PEG-modified glycol lignin in a larger reaction system (100 g of sample/1.0 L of the reaction solution) under pressurized O2 (0.7-2.5 MPa). In spite of the increased reaction scale, high vanillin yield (6.4 wt%) was maintained, compared to the vanillin yield (7.0 wt%) obtained in the above 14 mg/2.0 mL scale.

Keywords: Vanillin, Tetrabutylammonium hydroxide, Oxidation, Alkali, PEG-modified glycol lignin

2018-112

Effect of pretreatment on catalytic depolymerization of lignin in ionic liquid-solvent mixture

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Abstract: Pyridinium-based and imidazolium-based ionic liquids with different anions were synthesized and tested for the dissolution and subsequent extraction of lignin. Among used ionic liquids, pyridinium-based ionic liquids showed higher dissolution capacity than imidazolium-based ionic liquids at 80 ℃. Through extraction of lignin from alkali lignin-[Apy]Cl solution with different antisolvents, the results indicate that water and acetonitrile were promising ones and 97.3% recovery of lignin gotten from red pine. Furthermore, a continuous flow fixed-bed reaction system was developed to study the catalytic depolymerization of lignin at a low temperature using ZrO2/SO42− as the catalyst, and lignin-[Apy]Cl solution as the feedstock. Due to the pretreatment by [Apy]Cl, lignin was more readily decomposed in the reactor at low temperature. As expected, the phenolic compounds were the primary compounds observed in the identified compounds at 210 °C.

Keywords: ionic liquid; lignin; lignocellulose; pretreatment; catalytic depolymerization

2018-113

t-ブチルアルコールを用いた硫酸リグニンの熱可塑性制御

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Control of thermoplasticity of sulfuric acid lignin using t-butyl alcohol

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Abstract: Saccharification of woody biomass with concentrated sulfuric acid has been studied for a long time to obtain monosaccharides. The monosaccharides can be converted to bioethanol and other chemicals by fermentation. In this process, lignin is obtained in a high yield, as we call "sulfuric acid lignin" or "Klason lignin". It is very difficult to utilize this lignin because of poor solubility to organic solvents and thermal fusibility. In this work, t-butyl alcohol was added in the process. t-Butyl cation is expected to be created from t-butyl alcohol in acidic conditions and the self-condensation could be prevented by t-butylation of C6 position in lignin. Hinoki wood meal, water, t-butyl alcohol, and 95 % sulfuric acid were mixed and reacted in different ratios to control the thermoplasticity of sulfuric acid lignin. The reaction mixture was stirred at mainly 40 °C or other temperatures until it becomes creamy. Then, the reaction mixture was diluted, boiled and the acid insoluble fraction was recovered. Thermomechanical analysis showed that the treatment with a larger amount of t-butyl alcohol improved thermoplasticity of lignin. Reaction temperature accelerated the reaction rate, however, hardly effected on the thermoplasticity. As the reaction time was extended, apparent yield of lignin was increased with improved thermoplasticity. Isobutylene-based polymer was formed from t-butyl alcohol during longer reaction time and may have worked as a plasticizer.

Keywords: saccharification, concentrated sulfuric acid, t-butyl alcohol, self-condensation, thermoplasticity

2018-114

Synthetic studies of arabinoxylans – a lignin-hemicellulose junction in plant cell walls

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Abstract: Plant cell walls are structurally complex and contain a large number of diverse carbohydrate polymers, glycoproteins, polyesters and the complex polyphenol lignin. These plant materials are a highly valuable bio-resource and the focus of food, energy and health research. We are interested in studying the interplay of plant cell wall carbohydrates with proteins such as enzymes, cell surface lectins, and antibodies. We are studying the junctions between different components of the wall, such as carbohydrates–polyesters and lignin–hemicellulose. However, detailed molecular level investigations of such interactions are hampered by the heterogeneity and diversity of the polymers of interest. To circumvent this, we target well-defined oligosaccharides with representative structures that can be used for characterizing protein-carbohydrate binding and the interactions between glycans and other polymers in the wall. The presentation will highlight chemical syntheses of hemicellulose oligosaccharides from the group and some perspectives on current and future studies of carbohydrate functions in the cell wall.

Keywords: cell wall, hemicellulose, oligosaccharides

2018-115

Investigating cell cooperation during lignification

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Abstract: The amounts and compositions of lignin deposited in plant cell walls vary spatially between species, tissues, cell-types and cell wall layers as well as temporally during the differentiation of cell-types and development of tissues. Among the lignified cell-types, tracheary elements (TEs) are dead cells that accumulate large amounts of lignin in their secondary cell walls to conduct the hydro-mineral sap throughout the plant body. To maintain their vascular function during plant growth, dead TEs gradually reinforce their secondary cell walls with the addition of lignin. Using inducible cell suspension cultures and whole plants, the molecular and cellular mechanisms regulating the post-mortem lignification of TEs were investigated. This unique process allowing the adaptation of TE conductive properties is due to (i) the presence of phenoloxidases (laccases and/or peroxidases) in distinct cell wall layers, together with (ii) the cooperative supply of different lignin mono/oligomers produced by surrounding cells.

Keywords: post-mortem lignification, tracheary elements, zinnia

2018-116

バクテリアにおけるリグニン由来芳香族化合物の取り込みシステム

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Bacterial inner and outer membrane transport systems for a lignin-derived aromatic compound

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Abstract: In order to efficiently convert lignin-derived aromatic compounds into value-added chemicals, the complete elucidation of the uptake systems for lignin-derived aromatics is essential. In this study, we identified and characterized the inner and outer membrane transporters of 5,5’-dehydrodivanillate (DDVA) in Sphingobium sp. SYK-6. Among the SYK-6 mutants of 67 putative major facilitator superfamily transporter genes, we found that a ddvK mutant lost its ability to grow on DDVA. The ddvK mutant was unable to uptake DDVA, and ddvK conferred the capacity to uptake DDVA on a host strain Sphingobium japonicum UT26S. These results clearly indicate that ddvK encodes the DDVA inner membrane transporter. Overexpression of ddvK in an SYK-6 mutant of the 2-pyrone-4,6-dicarboxylate hydrolase gene increased growth rate in DDVA and the amount of DDVA converted and PDC produced after 48 h by 1.35 and 1.34-fold, respectively. In general, outer membrane transport of aromatic compounds is achieved by utilizing passive transporters such as porins and substrate-specific channels. In the SYK-6 genome, there is only one porin gene which may be involved in aromatic uptake, and substrate-specific channel genes were not found. In contrast, there are 74 TonB-dependent receptor (TBDR) genes which are known to encode active outer membrane transporters of Fe3+ siderophore and vitamin B12. DNA microarray analysis revealed that the transcription of a TBDR gene designated tbtA was specifically induced during the growth of SYK-6 on DDVA. The growth of a tbtA mutant on DDVA was significantly retarded, and its conversion rate of DDVA was also reduced. Furthermore, the uptake of DDVA by the tbtA mutant was significantly diminished. All these results indicate that tbtA is involved in the outer membrane transport of DDVA.

Keywords: Gram-negative bacteria, biphenyl, uptake system, inner membrane transporter, outer membrane transporter

2018-201

フェノール酸化活性を誘導する白色腐朽菌–細菌間相互作用の解析

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Induction of phenol oxidative activity resulted from interaction between white rot fungus and bacteria

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Abstract: To elucidate the mechanism for improvement of ligninolytic activity of Phanerochaete sordida in fungal-bacterial consortia retaining broad range of bacterial diversity, we experimented the several cultivation methods to simplify the bacterial diversity. On wood-agar medium containing guaiacol, fungal-bacterial consortia culture showed unusual coloration pattern resulted from phenol oxidation which was never seen in P. sordida single culture. On wood-agar medium containing guaiacol, fungal-bacterial consortia culture showed unusual coloration pattern resulted from phenol oxidation which was never seen in P. sordida single culture. And the consortia expressed phenol oxidation on PDA although P. sordida did not show phenol oxidative activity on PDA. Manganese peroxidase and laccase were involved in this phenol oxidation. The result of hyphal-bacterial attachment assay was dramatically reduced bacterial diversity in the consortia, and indicated that this promotion of phenol oxidation was caused by hyphal-adhesive bacteria. Now, we are trying to disclose the bacteria strain interacting to P. sordida and the relationship between the ligninolytic activity and this promotion of phenol oxidation.

Keywords: white rot fungi, microbial consortia, fungal-bacterial interaction, phenol oxidation, manganese peroxidase

2018-202

白色腐朽菌による木質バイオマスからの好気的水素産生に関する生化学的研究

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Biochemical studies on aerobic hydrogen production from woody biomass by white-rot fungi

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Abstract: We investigated for hydrogen production activities of 108 fungi obtained from decay wood, consequently slight but clear hydrogen production were observed from decaying wood meal cultures with Phanerochaete spp. and Trametes spp. fungi. By heterologous expression of putative hydrogenase genes from P. sordida and T. versicolor in Escherichia coli, these gene products showed hydrogen evolution activity. T. versicolor could produce hydrogen under aerobic condition, and it was suggested that this hydrogen evolution was catalyzed by fungal hydrogenase which accepts electrons from the formate dehydrogenase reaction by several experiments using with calcium carbonate. Discover of aerobic hydrogen production and hydrogenase activity of aerobic fungi are completely new findings in microbiology.

Keywords: white-rot fungi、aerobic hydrogen production、hydrogenase、formate dehydrogenase

2018-203

Phanerochaete chrysosporium によるアセタミプリド分解機構及び細菌共培養による分解促進機構の解明

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Elucidation of the degradation mechanism of acetamiprid by Phanerochaete chrysosporium and its improvement effect by co-cultivation with bacteria

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Abstract: Acetamiprid (ACE) is a member of the neonicotinoid insecticides, which have been widely used worldwide over the last two decades. However, their hazardousness, neurotoxicity to human and the potential toxicity to nontarget insect such as honeybees, is pointed out. Therefore, the ACE degradation potential of the white-rot fungus Phanerochaete chrysosporium was investigated. After incubation for 21 days at 30 ºC, P. chrysosporium degraded 32.1% of ACE in nutrient rich liquid culture. In addition, we identified a cytochrome P450 isozyme involved in ACE degradation by heterologous expression of CYPs cDNA derived from P. chrysosporium in yeast. Moreover, the promotion of ACE degradation of P. chrysosporium by co-cultivation system with bacteria isolated from nature environment was attempted. As a result, co-cultures with several bacteria that have no ACE degradation activity in pure culture showed higher ACE degradation (32.4-78.6%) than P. chrysosporium pure culture. Furthermore, almost all of these co-cultures were accumulated one of ACE degradation products resulting from the CYP reaction. Therefore, it was suggested that the bacteria showing higher ACE degradation in co-culture improved the CYP activity of P. chrysosporium to promote higher ACE degradation.

Keywords: Phanerochaete chrysosporium, neonicotinoid, bioremediation, co-culture, bacteria

2018-204

真菌グルクロン酸エステラーゼ(FGEs)ーリグニン・多糖結合体分解酵素ーの系統解析および白色腐朽菌の二つの FGE の発現と活性解析

◯林孟宜 1,2)、檜山明穂 2)、近藤敬子 1)、坂井勇太 2)、永田崇 1, 2)、片平正人 1, 2)
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Classification of a fungal glucuronoyl esterases (FGEs), lignin-carbohydrate complex (LCC) degradation enzymes, and expression/characterization of two novel FGEs of white rot fungi

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Abstract: In woody biomass, lignin is linked to hemicellulose by covalent bonds such as ester, ether, and phenyl-glycoside bonds to form lignin-carbohydrate complex (LCC). Fungal glucuronoyl esterases (FGEs) catalyze cleavage of the ester bond connecting a lignin alcohol to the xylan-bound 4-O-methyl-D-glucuronic acid of glucuronoxylans. Thus, FGEs have potential for woody biomass utilization. In this study, we built a phylogenetic tree from almost four hundred putative FGEs and defined six main clades. The putative FGEs belonging to one of the clades were found to have higher theoretical isoelectric points than those in the other five clades. To gain a molecular insight into the putative FGEs in the uncharacterized clades, we expressed two FGEs originated from Ceriporiopsis subvermispora (CsGE) and Pleurotus eryngii (PeGE) using Pichia pastoris. Both CsGE and PeGE exhibit esterase activity, the activity of PeGE being highest among reported FGEs. PeGE was found to exhibit high tolerance toward various reagents, which are often used to dissolve woody-biomass extracts and/or degrading enzymes; this finding may make PeGE a potentially more applicable enzyme for utilization of wood biomass.

Keywords: Glucuronoyl esterase; Fungi; Lignin-carbohydrate complex; Benzyl glucuronic acid

2018-205

リグニン芳香核組成を改変した組換えイネ株のバイオマス利用特性解析

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1) 京大生存研、2) 京大院農、3) 京大生存基盤展開

Comparative characterization of lignocellulose usability of transgenic rice plants altered in lignin composition

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Abstract: Aromatic composition of lignins has been considered to be an important structural trait that affects the physico-chemical properties of lignocellulosic biomass. However, our knowledge regarding the relationship between the lignin aromatic composition and biomass utilization characteristics is still considerably limited especially in monocotyledonous grass species despite their potential as biomass feedstocks. Here, we used our recently generated transgenic rice with distinct lignin monomer composition, i.e., guaiacyl (G)/syringyl (S)/p-hydroxyphenyl (H) aromatic unit ratio, to investigate the effect of altered lignin composition on their biomass saccharification efficiency and heating value. The H-lignin-enriched transgenic rice showed significantly enhanced biomass saccharification efficiency without any pretreatment or with alkali and acid pretreatments, whereas the S-lignin-enriched transgenic rice showed further enhanced saccharification efficiency when using liquid hot water pretreatment. While no significant differences in the biomass heating values between the transgenic rice materials tested, analysis of synthetic lignins comprising only G, S or H units suggested that increasing H or G units may be beneficial to increase the heating value of biomass.

Keywords: Oryza sativa, Coniferaldehyde 5-hydroxylase, p-Coumaroyl ester 3-hydroxylase, Enzymatic saccharification, Heating value

2018-206

β-O-4 還元的開裂産物β-hydroxypropiovanillone のバクテリアにおける代謝経路

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Bacterial catabolism of β-hydroxypropiovanillone produced by the β-O-4 reductive cleavage

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Abstract: The β-O-4 cleavage is a crucial step in lignin biodegradation. A bacterial β-O-4 cleavage pathway and catabolic genes have been most elucidated in Sphingobium sp. strain SYK-6. In this strain, four stereoisomers of β-O-4 type biaryls, guaiacylglycerol-β-guaiacyl ether (GGE), are stereospecifically degraded into achiral β-hydroxypropiovanillone (HPV) by the β-etherase enzyme system. To date, a similar system for β-O-4 reductive cleavage has been found in several bacteria and most recently in fungi, however there is no report for the HPV catabolism. In this study, we determined the HPV and HPS (a syringyl-type HPV analog) catabolic pathway in SYK-6 and characterized the genes involved in part of the pathway. In SYK-6 cells, HPV was subjected to two steps of oxidation and converted into vanilloyl acetic acid (VAA) via vanilloyl acetaldehyde (VAL), and the resultant VAA was further catabolized via vanillate. HPS was also degraded by the same pathway. A gene encoding glucose-methanol-choline oxidoreductase family enzyme, SLG_12830 (hpvZ), was isolated as an essential gene for conversion of HPV and HPS from genomic library screening. The localization of HpvZ in SYK-6 was determined to be both the cytoplasm and membrane. For the oxidation of HPV, HpvZ showed ability to use ubiquinone derivatives as electron acceptors. Among 23 aldehyde dehydrogenases (ALDH) of SYK-6, thirteen enzymes were able to oxidize VAL into VAA. Mutant analyses suggested that multiple ALDH genes, including SLG_20400, involved in the oxidation of VAL.

Keywords: Gram-negative bacteria, β-aryl ether, phenylpropane, coniferyl alcohol, ubiquinone,

2018-207

人工的な細胞壁再構築系でリグニンの効果を見る

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Evaluating the contribution of lignin to the cell wall properties by using a system to reconstitute artificial cell wall in planta

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Abstract: Contribution of lignin to the cell wall properties is not necessarily well described due to lack of mutant which doesn’t have any lignin in secondary cell walls. Because lignin is inevitable for vascular vessels to keep water inside and its biosynthesis is tightly coregulated in vascular vessels and fiber cells, it is difficult to obtain the mutant mentioned above which could grow relatively normal. We found before Arabidopsis double mutant of NST1 and NST3 which doesn’t have any secondary cell walls in stem fiber cells (Mitsuda et al., 2007). We aimed to isolate new transcription factor genes which could reconstitute a part of or entire secondary cell walls in this mutant by screening many transcription factor genes (Sakamoto and Mitsuda 2015). We finally found that ClassIIId and IIIe ERF transcription factors can produce thick unusual cell walls which don’t have any lignin in the mutant fiber cells when they are expressed under the control of NST3 promoter which is

specifically active in fiber cells (Sakamoto et al., 2018). The accumulated cell walls are very similar to primary cell walls in terms of monosaccharide composition and gene expression profile (Sakamoto et al., 2018). We then additionally expressed MYB58 transcription factor in the fiber cells of the transgenic lines and succeeded to deposit lignin on the accumulated primary cell wall-like cell walls. By observing the fiber cells with electron microscope and testing stem mechanical properties, we now demonstrated that lignin confers mechanical strength to the cell walls in cell-order level and in tissue-order level.
Keywords: lignin, mechanical property, plant cell wall, transcription factor

2018-208

植物細胞壁におけるリグニンエンジニアリングのための新規酵素遺伝子の探索

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Exploring of useful enzymatic genes for lignin engineering

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Abstract: Lignins are aromatic polymers which are largely present in secondary cell wall and provides plant critical roles such as physical force in supporting tissue and hydrophobicity in vascular tissues. However, its recalcitrance hampers the industrial use for the production of biofuel and biomaterials and therefore, lignin engineering has potential to improve the processing efficiency of these production. We screened ca. 50 transgenic plants which expressed various enzyme genes, products of which convert metabolites of monolignol biosynthetic pathways, under the control of a Populus Kitakamiensis C4H promoter and identified some transgenic plants showed apparent abnormalities in xylem fibers and vessels by Wiesner and Mäule staining. We further analyzed to their cell wall characteristics of those transgenic plants. One of them showed 2-hold higher saccharification efficiency by cellulose treatment than wild-type plant while monosaccharide amount and composition in it were almost comparable to those in wild-type. Furthermore, H monomer ratio in cell wall of the transgenic plants is 50 times higher than that in wild-type. These results indicated that this approach is powerful tool to identify the gene which improves cell wall digestibility by modifying lignin structure.
Keywords: lignin engineering, molecular breeding, plant cell wall

2018-209

リグニン生合成抑制型転写因子 OsMYB108 変異イネの解析

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Characterization of transgenic rice with disrupted function of OsMYB108, a transcriptional repressor in lignin biosynthesis

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Abstract: Grass biomass crops, such as Erianthus spp. and Sorghum spp., which typically show higher lignocellulosic biomass productivity than trees, represent potent biomass feedstocks for producing biofuels and various biomass-derived materials. Lignins, a major component of lignocellulose, have a positive impact on the biomass heating value, and also represent a viable source of aromatic chemicals. Thus, breeding approaches to enrich lignins in grass biomass crops can be beneficial for establishing a cost-effective biorefinery processes. In this study, we generated lignin-enriched rice (Oryza sativa) transgenic lines through the CRISPR/Cas9-mediated targeted mutation of OsMYB108, a transcriptional repressor gene involved in lignin biosynthesis, and closely characterized their lignocellulose structure by chemical and NMR analyses.

Keywords: Genome editing; Heating value; Molecular breeding; Mutagenesis; Transcription factor

招待講演

Designing Lignins for the Biorefinery

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Abstract: Lignin is crucial to plant growth and development but is problematic due to its major impediment to biomass utilization in various processes. It is, however, increasingly recognized that valorizing lignin is essential for sustainably and profitably converting biomass to valuable products. Researchers are now able to contemplate altering lignins for improved utilization in a biorefinery and ponder what constitutes an ‘ideal lignin’ for processing and conversion.

As lignin is a polymer formed from its monomer radicals by purely chemical radical coupling react¬ions, the breadth of options for ‘designing’ the com¬position and structure of lignins is unparalleled. Beyond simply manipulating the relative levels of the traditional monolignols, new phenolic monomers can be introduced into the polymer, subject solely to the plant’s ability to produce and transport them to the wall and their chemical compatibility with the com¬ponents and (cross-) coupling reactions that typify lignification. Recent examples of this metabolic plasticity include demonstrating the introduction of hardwood-type lignins into soft¬woods to improve pulping performance, and the identification of plants producing lignins composed almost entirely of hy¬droxy¬cinnamaldehydes, opening up new and unique derivatization and modification op¬por¬tun¬ities. Tissues containing 100% levels of caffeyl or 5-hydroxy¬coniferyl alcohol-derived lignin polymers have been discovered. These two catechol-type monolignol analogs produce almost homo¬geneous (single-structured) linear lignin chains upon poly¬mer-ization, again creating opportunities for valuable new uses for lignin. The recently discovered catechyl lignin (C-lignin), which is essentially a benzodioxane homopolymer, might represent an ideal lignin for lignin valorization. We discovered that C-lignin is highly acid resistant and is able to maintain its native structure after harsh acidic treatments. Its hydrogenolysis resulted in the cleavage of all benzodioxane structures to cleanly produce catechyl-type monomers in essentially quantitative yield. Lignins have also now been suc¬cess¬fully ‘redesigned’ to contain readily chemically cleav¬able ester bonds in the polymer backbone, facilitating improved industrial processing – for example, chem¬ical pulping, or pretreatment options for the sacc¬har-ification of wall polysaccharides to sugars for liquid biofuels production. Inspired by Nature’s incor¬poration of the non-lignin-pathway flavonoid, tricin, into monocot lignins, researchers can now also con¬template plants in which the lignins incorporate valuable components that can be subsequently retrieved from the ‘waste’ streams. We suspect that we are now entering a reinvig-oration period for lignin research aimed at its manip¬ulation for improved utilization.

Keywords: Lignification, metabolic plasticity, monolignol, gene misregulation, engineering, pulping, C-lignin

特別講演

β-O-4 構造を中心としたリグニン化学構造の多様性と規則性、および、それらの化学的反応性との関係

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Variety and regularity of lignin chemical structure, especially of β-O-4 structure, and, the relationships between the chemical reactivity

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Abstract: Hardwood lignins and softwood lignins are different by the presence of syringyl type aromatic nuclei in the former. In addition, there are wide varieties in the lignin characteristics (structure and amount) depending on wood species, environment of growing site, portion in the wood, portion in the cell wall, and so on. However, clear tendencies are also observed in the variety of lignin characteristics by taking the syringyl/guaiacyl ratio as an index. We have shown that the lignin chemical structure has a significant effect on the chemical reactivity such as delignification during chemical pulping. In this report, I review the recent achievements of my laboratory about the quantitative relationships between lignin structure and reactivity.

Keywords: molecular structure, reactivity

2018-P01

SEC/MS および分取 SEC/MALDI-TOFMS によるリグニンの分子量測定法

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Molecular weight determination of lignin by SEC/MS and preparative SEC/MALDI-TOFMS

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Abstract: To analyze the molecular weight of lignin, the conventional SEC/RI analysis had the problem that the results fluctuate greatly due to the difference in mobile phase and column. In order to establish a molecular weight determination method by SEC/MS, mobile phase conditions suitable for MS ionization were studied. As a result, it was confirmed that SEC/MS has low molecular weight components with molecular weight of about 2400, and that of preparative SEC/MALDI-TOFMS has high molecular weight components with molecular weights of up to 30000, almost coincide with calibration curves based on polystyrene (PSt) .

The results of this research were obtained from NEDO (New Energy and Industrial Technology Development Organization) outsourcing projects.

Keywords: Cedar, Eucalyptus, GPC, CAD, UV

2018-P02

熱機械分析によるリグニンの軟化温度測定

〇平野孝行、大田玲奈、北川雅士、畠幹生、大川朋寛、高井良浩
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Softening temperature of lignin by thermomechanical analysis

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Abstract: We investigated the measurement condition of softening temperature of the lignin by the TMA method using commercial organosolv lignin. As a result, the sample formed using a press machine could measure change in dimensions with softening. Based on an investigated result, we measured that the softening temperature of hardwood lignin and softwood lignin. The softening temperature of hardwood lignin and softwood lignin were approximately 170℃ and 140℃, respectively. The softening behavior accorded with the sample appearance change by the real-view type thermal analysis result. In addition, at 7 mass% of moisture content, the difference was not recognized to softening temperature with the hardwood lignin, the softwood lignin either.

Keywords: Cedar, Eucalyptus, TMA, Softening temperature, moisture

2018-P03

初期熱分解生成物の低減を目指したコルクの加熱脱着 GC/MS 分析

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Thermal desorption-GC-MS analysis of cork: aiming to reduce the amount of initial pyrolysis products

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Abstract: Cork was analyzed to reduce the amount of initial pyrolysis products by thermal desorption-GC-MS.

Assuming that acetic acid, which occurs due to the hydrolysis of acetyl group existing in cork, causes a decline in heat resistance, we pretreated cork to hydrolyze acetyl group in alkaline solutions. Specifically, cork particles were heated at 50˚C for 16 hours in the water where there were calcium hydroxide, magnesium hydroxide, aluminium hydroxide excessively. It was found from the experimental results that vanillin and furfural as well as acetic acid decrease by alkaline pretreatments.

Keywords: cork, thermal desorption-GC-MS, acetic acid, hemicellulose, degradation mechanisms

2018-P04

選択的 13C 標識法を用いたリグニンの構造解析 - INADEQUATE 測定による検討 -

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Structural analysis of lignin by 13C-enrichment technique -Investigation by INADEQUATE measurement-

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Abstract: Among the interunit linkages in lignin, investigation of β-5, β-β, and 5-5 linkages is very important for effective utilization of lignin because their bonds are very strong. In this study, we focused on the carbon at β-position and analyzed their structure by NMR measurement in an INADEQUATE mode. This method is powerful for the analysis because it can measure 13C-13C linkage directly. However, there is few report to analyze the structure of lignin using the INADEQUATE mode because of low presence ratio of 13C resulting in low sensitivity. In this study, selective 13C enriched DHP at β-position was synthesized and measured by the INADEQUATE mode to analyze the structure of lignin related to β-carbon.

Keywords: NMR, INADEQUATE mode, DHP, selective 13C-enrichment technique, β-carbon

2018-P05

13CO2 投与によるイチョウリグニン芳香核構造の解析

〇宮田苑加 1)、青木弾 1)、松下泰幸 1)、竹内美由紀 2)、福島和彦 1)
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Analysis of lignin aromatic structures in Ginkgo biloba by 13CO2 administration

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Abstract: Lignin is one of the major plant cell wall polymers. Despite extensive investigation, the structure is not completely understood. In order to elucidate the lignin structure, 13C-enriched lignin was produced by an administration of 13CO2 to Ginkgo biloba wood under airtight condition and analyzed by a high lateral resolution secondary ion mass spectrometry (NanoSIMS) and 13C-NMR measurements. As a result of NanoSIMS, the 13C ratio was up to 60 % in the xylem cell wall. As for solution-state 13C-NMR spectrum, we assigned the major lignin aromatic carbons and quantified their frequencies.

Keywords: structural analysis, 13CO2 administration, NanoSIMS, solution-state NMR, quantitative determination

2018-P06

分析的熱分解法による酸加溶媒分解スギリグニンの組成分析

〇京極未憂 1)、中川明子 1)、ネーティティ 2)、髙田依里 2)、山田竜彦 1,2)
1)筑波大学、2)森林総合研究所

Chemical composition analysis of polyethylene glycol (PEG) solvolysis lignin by pyrolysis gas chromatography · mass spectrometry (Py - GC / MS)

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Abstract: The process of acid-catalyzed PEG solvolysis of Japanese cedar to produce polyethylene glycol (PEG) solvolysis lignin (glycol lignin) has being developed at FFPRI in order to promote an effective utilization of woody biomass. It was revealed that glycol lignin included ether-bonded PEGs as well as carbohydrate derived furan-based polymer. However, the furan-based polymer has not been analyzed quantitatively. In this study, Py-GC/MS analysis was conducted to evaluate the content of bonded PEG and furan-based polymer of glycol lignin.

Keywords: solvolysis, lignin, pyrolysis, PEG, furan

2018-P07

針葉樹単離リグニンの分子量分画とビフェニル型構造の分布

〇羽田尚希１）、秋山拓也１）、横山朝哉１）、松本雄二１）
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Fractionated Softwood MWLs Depending on the Solubility in Dioxane, and Their Molecular Weight Distribution and Biphenyl Contents

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Abstract: Japanese red pine milled wood lignin (MWL) was fractionated based on the difference in the solubility in 1,4-dioxane containing different proportion of diethyl ether. Obtained six fractions were subjected to size exclusion chromatography and alkaline nitrobenzene oxidation to investigate the relationship between the molecular weight distribution and the composition of inter-unit linkage, i.e. non-condensed type, β-5 type and biphenyl type.

Keywords: 5-5 linkage, lignin, alkaline nitrobenzene oxidation, divanillin, gymnosperm

2018-P08

種々の褐色腐朽菌で腐朽させた木材の化学的特性

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Chemical properties of wood samples decayed by brown-rot species

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Abstract: Brown-rot fungi are at least distributed into the four orders of Boletales, Dacrymycetes, Gloeophyllales, and Polyporales. Therefore, we hypothesized that there are differences in wood degradation manner among brown-rot fungi which belong to different evolutionary groups. To obtain the knowledge on the diversity of wood degradation manner in brown-rot fungi, structural features of wood samples, which were decayed by four different brown-rot fungi, were investigated with FT-IR.

Keywords: brown-rot fungi, wood decay, lignin, polysaccharide, FT-IR

2018-P09

Characterization of heat treated glycol lignins produced by acid-catalyzed polyethylene glycol (PEG) solvolysis

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Abstract: In this study, three types of polyethylene glycol (PEG400)-modified glycol lignin, GL400L, GL400M, and GL400S samples were subjected to heat treatment from 100ºC to 160ºC in constant temperature oven for 1 h and the effect of heat treatment temperature on properties of the resultant GL samples were investigated, including thermal analyses (glass transition temperature, Tg, thermal flow temperature, Tf, decomposition starting temperature, Tdst), molecular (Mw, and Mn), and structural (thioacidolysis analysis and ATR-FTIR) analyses. Overall, there are small changes on thermal behavior and structural properties of the heat treated GL samples, which in turn depend on the molecular mass of the respective control GL sample and the source wood meal size from which control GL sample was produced.

Keywords: glycol lignin, polyethylene glycol (PEG) solvolysis, wood meal size, heat treatment

2018-P10

改質リグニンを用いた柔軟性エポキシ樹脂の合成と物性評価

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Fabrication and properties of Flexible Epoxy Resin using Glycol Lignin from Softwood

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Abstract: An epoxy resin with high lignin content has been successfully prepared by mixing and thermal curing of Glycol Lignin and an aliphatic epoxy material, polyethylene glycol diglicidyl ether (PEGDGE), without using additional solvent. Mechanical properties of the resins with different lignin contents were evaluated, and it was found that the resins had good flexibilities and elasticities dependent on the Glycol Lignin content. Mechanism of the curing reaction was also discussed through the chemical equivalent weight between Glycol Lignin and PEGDGE.

Keywords: glycol lignin, softwood, polyethylene glycol, epoxy resin, curing reaction

2018-P11

テトラブチルアンモニウムヒドロキシド中での PEG 改質リグニンからのバニリン生産における温度および圧力の影響

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Effects of Temperature and Pressure on Vanillin Production from PEG-modified Glycol Lignin in Tetrabutylammonium Hydroxide

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Abstract: Aerobic oxidation of lignin in tetrabutylammonium hydroxide (TBAH) produces vanillin and its related phenols with high selectivity. We performed vanillin production from PEG-modified glycol lignin in a larger scale reaction system (100 g of sample/1.0 L of the reaction solution) under pressurized O2 (0.7-2.5 MPa) at temperatures of 80-120 oC. Under the optimum conditions (120 oC/2.5 MPa/1.0 h) vanillin was obtained in 6.1 wt% yield, which was comparable to that (7.0 wt%) obtained in our previous small scale (14 mg of sample/2.0 mL of the reaction solution) experiment.

Keywords: PEG-modified glycol lignin, oxidation, vanillin, tetrabutylammonium hydroxide, larger scale reaction

2018-P12

イオン液体前処理と酵素糖化により得られる残渣リグニンの特性評価

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Oxidative depolymerization potential of biorefinery lignin obtained by ionic liquid pretreatment and subsequent enzymatic saccharification of biomass

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Abstract: This study compared the oxidative depolymerization potential between ionic liquid (IL)-pretreated/enzyme lignin, diluted acid (DA)-pretreated/enzyme lignin, and soda lignin of eucalyptus, by means of alkaline nitrobenzene oxidation which depolymerize lignin into phenolic aldehydes such as vanillin and syringaldehyde. Here, the IL-pretreated/enzyme lignin was prepared by 1-ethyl-3-methylimidazolium acetate pretreatment and subsequent enzymatic saccharification. Upon the oxidative depolymerization of lignin sample by alkaline nitrobenzene oxidation, total yield of vanillin and syringaldehyde was 36.6% for untreated control eucalyptus. In contrast, the yield was enhanced upto 48.0% for IL-pretreated/enzyme lignin. As for the soda lignin prepared by alkali cooking, the yield was 29.0%. As for the DA-pretreated/enzyme lignin prepared by DA pretreatment and subsequent enzymatic saccharification, the yield was 39.5%. Therefore, it was found that the IL-pretreated/enzyme lignin showed the highest yield of phenolic aldehydes (vanillin and syringaldehyde) via alkaline oxidation, namely, highest oxidative depolymerization potential among the lignin tested.

Keywords:Ionic liquid, Pretreatment, Enzymatic residue lignin, Oxidative depolymerization, Phenolic aldehydes.

2018-P13

有機水酸化物水溶液に溶解した木粉成分の酸添加による分画

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Addition of acids to organic hydroxide aqueous solution for the fractionation of woody biomass

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Abstract: Lignocellulosic biomass is the most abundant renewable resource on the earth. The main components of lignocellulosic biomass are cellulose, hemicellulose, and lignin. We have previously reported several ionic liquids for the efficient dissolution of these valuable components, and also proposed that tetrabutylphosphonium hydroxide (TBPH) aqueous solution as a novel solvent of woody biomass under mild condition. In this study, fractionation of woody biomass dissolved in TBPH aqueous solution was examined. Neutralization of TBPH aqueous solution with acids yields mixture of phosphonium type ionic liquids and water, and the mixture was expected to dissolve only lignin fraction.

Keywords: Organic hydroxide aqueous solution, ionic liquids, fractionation, neutralization,

2018-P14

鉄触媒を用いる木質リグニンの酸化分解反応

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Iron-Catalyzed Oxidative Depolymerization of Lignin

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Abstract: An iron complex bearing bis(trifluoromethanesulfonyl)amido ligands showed high catalytic activity for oxidative degradation of lignin dimer models and depolymerization of soda lignin. An X-ray micro CT analysis has revealed that the iron complex-catalyzed decomposition of the wood tissues proceeds at the surface of tracheids and at the pit borders, where efficient and direct contact of the iron catalyst and oxidant promotes the depolymerization of lignin incorporated in the secondary wall.

Keywords: degradation, oxidation, iron catalyst, β-O-4, 3D imaging

2018-P15

リグノスルホン酸の酸糖化触媒としての特性

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Lignosulfonic Acid as Catalysis for Acid Saccharification

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Abstract: Lignosulfonic acid, which is the most available industrial lignin produced from sufite pulping process, was verified as saccharification catalysis of woody biomass. Saccharification rate of birch wood was faster than that of Sugi wood. More than 40% (w/w) of birch wood was decomposed by saccharification using lignosulfonic acid at 150 °C for 6 h. By contrast, decomposition of Sugi wood meal was ~30% under the same saccharification conditions. In our previous study for acid saccharification of disaccharide, Xylobiose was readily hydrolyzed by lignosulfonic acid in compare with cellobiose. Therefore, observed difference in the saccharification rate would be related to the differerences in the mono-sugar compositions between birch and sugi woods.

Keywords: Lignosulfonic acid, Acid catalyst, Acid hydrolysis

2018-P16

量子化学計算を用いたアルカリ性ニトロベンゼン酸化における分子機構の解明

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Quantum Chemical Study on Mechanisms in Alkaline Nitrobenzene Oxidation

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Abstract: Molecular mechanisms in alkaline nitrobenzene oxidation (AN oxidation) of lignin – in spite of its importance in lignin chemistry – have not been fully clarified yet. This study carried out DFT(M06-2X)-level calculations for degradation of p-hydroxyphenyl type trans-enol ether EE with nitrobenzene, where EE was formed through alkaline degradation of phenolic □-O-4 structures and considered to be a major intermediate in the AN oxidation of phenolic □-O-4 structure. Our computational results suggested that two-electron oxidation of EE occurred though electrophilic attack of nitrobenzene on the □-positon of the EE's side chain. Pathways involving complexation between the phenolic OH of EE and nitrobenzene were not likely as such complexes were not optimized as stable structures.

Keywords: Alkaline nitrobenzene oxidation, quantum chemical calculation, density functional theory (DFT), vanillin, mechanisms

2018-P17

過酸化水素漂白反応を用いたリグニン由来の芳香族アルデヒドおよび芳香族酸生成最適条件の探究

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Study on the optimal conditions to generate lignin-derived aromatic aldehyde and acid under hydrogen peroxide bleaching conditions

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Abstract: A non-phenolic β-O-4-type lignin model compound, veratrylglycerol-β-guaiacyl ether (VG), was treated with stepwisely-added H2O2 under alkaline H2O2 bleaching conditions. The purpose of this treatment was to develop optimal reaction conditions to produce lignin-derived aromatic aldehydes and acids from non-phenolic lignin units by the use of active oxygen species produced by the self-decomposition of H2O2. The examined reaction parameters were alkaline concentration, temperature, number of addition times of H2O2, amount of FeCl3 as a catalyst, and ratio of FeCl3 to MgCl2. Higher alkali concentration resulted in higher yield of aimed products and higher VG consumption under the condition examined. The effects of FeCl3 and MgCl2 addition were clearly shown and their doses and ratio significantly affected the yield of aimed compounds and VG consumption.

Keywords: Lignin; Veratraldehyde; Veratric acid; hydrogen peroxide bleaching

2018-P18

リグニンのアシドリシスにおけるフェノール性水酸基の重要性

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Significance of Phenolic Hydroxy Group in Lignin Acidolysis

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Abstract: The most common C6-C3-type phenolic β-O-4 lignin model compound, guaiacylglycerol-β-guaiacyl ether (I), was acidolyzed in an aqueous 82% 1,4-dioxane mainly using HCl, HBr or H2SO4 as an acid. The results were compared with those of the corresponding non-phenolic analogue, veratrylglycerol-β-guaiacyl ether (IV), obtained in our previous study to discuss the effect of the presence of the phenolic hydroxy group on the acidolysis reaction. Phenolic compound I was acidolyzed much more rapidly than non-phenolic compound IV in accordance with previous knowledge on the acidolysis. It was surprising, on the other hand, that the reaction route of phenolic compound I is not the same as that of non-phenolic compound

IV. Fairly amounts of the primary C6-C3-type Hibbert's ketone and its isomer were detected in the acidolysis of phenolic compound I using H2SO4, although in the same acidolysis of non-phenolic compound IV the major reaction product was exclusively the non-phenolic C6-C2-type Hibbert's monomer afforded by the liberation of the γ-hydroxymethyl group as formaldehyde. It was thus confirmed that the presence of the phenolic hydroxy group affects not only the rate but also mechanism of the acidolysis. The same comparisons were also performed using C6-C2-type phenolic and non-phenolic β-O-4 lignin model compounds.

Keywords: alkyl aryl ether, hydrobromic acid, hydrochloric acid, sulfuric acid

2018-P19

アルカリ性下におけるリグニンのキノンメチド構造生成に及ぼす芳香核構造の影響

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Effect of the type of aromatic nucleus on the formation of quinone methide structure in lignin under alkaline conditions

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Abstract: The purpose of this study is to examine the effect of the type of aromatic nucleus on the formation rate of quinone methide (QM) under alkaline pulping conditions by employing simple phenolic C6-C1-type compounds (methyl ether of p-hydroxybenzyl alcohol derivatives) carrying one or two functional groups at the meta- of the benzyl position. The formation rate of QM was in the order of the compounds carrying: di-CH3 > di-OCH3 (syringyl) > CH3 > OCH3 (guaiacyl) > none (p-hydroxyphenyl) > F > Cl. It was possible to consider that the electron donating or withdrawing effects of the functional groups promote or suppress the formation of QM, respectively. Because these effects of the functional groups are known to similarly promote or suppress oxygen oxidation of corresponding phenol derivatives under alkaline conditions, other simple C6-C1-type compounds analogous to the above were subjected to an oxygen oxidation and the order of their disappearance rates were compared with the above observed formation rate of QM. The oxidation rate was in the order of: di-OCH3 (syringyl) > di-CH3 > OCH3 (guaiacyl) > CH3 > none (p-hydroxyphenyl) > Cl. This order was similar to that of the formation rate of QM, except that the OCH3 group promotes the oxygen oxidation more than the CH3 group.

Keywords: methoxy group, substituent, electron donating ability, π electron system, oxygen-alkali

2018-P20

非天然型コニフェリンの合成と性質

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Synthesis and property of coniferin enantiomer

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Abstract: Coniferin enantiomer which is composed of L-glucose and coniferyl alcohol was synthesized by the conventional method. Coniferin enantiomer was not degradated by β-glucosidase, differing natural coniferin. Coniferin enantiomer showed the law membrane permeability. The result suggest glucose moiety of coniferin is important to the membrane permeability.

Keywords: coniferin, monolignol, lignin, enzyme, L-glucose

2018-P21

フェニルグリコシド型 LCC（リグニン－多糖複合体）解析用モデル化合物の合成

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Preparation of new phenyl glycoside-type LCC model compounds for NMR analysis of native LCC

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Abstract: New phenyl glycoside type LCC model compound (β-5 type dilignol glycoside 6) was prepared from β-5 type dilignol 1 by the four reaction steps (acetylation, selective deacetylation, glycosyration, deacylation). The key reaction in the synthetic route was glycosyration. Glycosyration between β-5 dilignol derivative 3 and glycocyl imidate 4 afforded β-glucoside exclusively. The synthetic method for compound 6 was applied to the syntheses of other LCC model compounds. The fully assigned NMR spectra of guaiacyl dilignol β-D-glycosides provided useful database information for the analysis of LC linkages in plant cell walls using high resolution NMR techniques.
Keywords: 2D-NMR, dilignol β-glycoside, hetero-nuclear single quantum coherence (HSQC), lignin-carbohydrate complex (LCC), phenyl glycoside

2018-P22

PEG-HRP を用いた有機溶媒中でのコニフェリルアルコールの脱水素重合

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Dehydrogenative Polymerization of Coniferyl Alcohol in Organic Solvents with PEG-HRP

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Abstract: Among the interunit linkages in lignin, a β-O-4 bond is one of the most important bonds. The frequency of the □-O-4 bond is about 50-60% in wood lignins. Whereas the frequency of the β-O-4 is low in an artificial lignin which is obtained by the dehydrogenative polymerization of monolignols in buffer solution. This may be partly attributed to the fact that the environment of lignin biosynthesis is more hydrophobic than the buffer solution because of the presence of hemicellulose in the cell wall. In this study, the dehydrogenative polymerization of coniferyl alcohol was conducted in aq. EtOH with HRP or PEG-HRP to better understand the effect of hydrophobic environment on lignin biosynthesis.
Keywords: hydrophobicity, polyethylene glycol, DHP, HSQC, GPC

2018-P23

ケナフコアから血圧抑制および抗糖化成分の検出

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Detection of lignin-derived components which have blood pressure suppression and antiglycation from Kenaf core

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Abstract: Kenaf core was hydrolyzed with water or 1 to 3 % of hydrogen peroxide solution. Obtained water-soluble compounds were estimated with antihypertensive effect and anti-glycation effect on collagen. Interestingly, both of effects were detected in all water soluble components from Kenaf core hydrolysis with water or hydrogen peroxide solution. These components contained some lignin-decomposed products. This study is suggested that a new lignin application which is a utilization of lignin-derived products as a functional component.
Keywords: lignocellulose decomposition, hydrogen peroxide, functional components, blood pressure suppressant, anti-glycation component

2018-P24

マイクロ波反応を用いたサトウキビバガスからの抗ウイルス活性物質の生産

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Production of Antiviral Compounds from Sugarcane Bagasse by Microwave Reactions

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Abstract: The process of converting lignocellulose into high value-added compounds as well as platform chemicals and fuels is strongly required for establishment of biorefinery. Sugarcane bagasse is one of the most abundant lignocellulosic agricultural residues, and promising feedstock for biofuels and chemicals. Our objective in the present study is production of antiviral compounds from sugarcane bagasse. Bagasse was decomposed by microwave reaction in several polar solvents with catalysis, and the degradation products were fractionated using several organic solvents. Antiviral activities against encephalomyocarditis virus (EMCV) of each fraction were evaluated by real-time polymerase chain reaction. The chemical structure of antiviral compounds was analyzed by pyrolysis-GCMS and NMR. The results suggested that the antiviral compounds are composed of polysaccharide and lignin and that the antiviral compounds directly inhibited the EMCV replication.

Keywords: Sugarcane bagasse, Microwave degradation, Antiviral agent, Lignin

2018-P25

リグニンだけを炭素源とした cis,cis-ムコン酸生産に効果的な培養要素の同定

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Identification of effective factors for sugar-free cis, cis-muconic acid production from lignin-related phenols

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Abstract: cis,cis-muconic acid (ccMA) is a platform chemical for polymer synthesis and thus bio-based ccMA production from carbohydrate such as glucose has been reported. In this study, we developed a new bacterial strain capable of producing ccMA from lignin-derived phenols, in which no carbohydrates were required for the source of carbon and energy. The engineered Pseudomonas putida strain could grow not only on vanillate or 4-hydroxybenzoate but also lignin extracts from Japanese Cedar, and produced ccMA without consuming sugar. Through this work, we revealed dissolved oxygen is an effective parameter in regulating ccMA yield and identified proper supply of nitrogen in addition to carbon source is necessary to maintain ccMA production in fed-batch culture mode.

Keywords: Softwood lignin, cis,cis-muconic acid, metabolic engineering, bio-based chemical, lignocellulosic biomass utilization

2018-P26

NMR 法によるリグニン-セルラーゼ糖質結合モジュール間吸着の解析

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Binding Analysis between Lignin and Carbohydrate Binding Module of Cellulase by NMR

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Abstract: Enzymatic saccharification of lignocellulosic biomass is expected to produce green chemicals. Industrially, a cellulolytic system including cellobiohydrolase I (Cel7A) from Trichoderma reesei has been widely used. Cel7A consists of catalytic domain and carbohydrate binding module 1 (TrCBM1) connected with highly glycosylated linker. TrCBM1 plays a role to enhance activity of Cel7A by bringing the catalytic domain in close to the cellulose. However, TrCBM1 has affinity to lignin, in addition to cellulose, and the resultant non-productive binding to lignin decreases efficiency of the saccharification. To date, the interaction mechanism between TrCBM1 and lignin has not been clearly understood. In this study, we analyzed interaction site of TrCBM1 with lignin at amino acid resolution using NMR. Binding site of TrCBM1 was analyzed by 1H-15N SOFAST-HMQC NMR with incremental titration of cellohexaose and milled wood lignin (MWL) from Japanese cedar and Eucalyptus globulus. The mechanism of the non-productive binding was discussed based on the binding analysis.

Keywords: Carbohydrate binding module, NMR, Cellulase, Chemical shift perturbation

2018-P27

褐色腐朽の観点からのリグニンが保持する第二鉄還元能の考察

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Iron-reducing capacity of lignin and the implication on the relationship with brown-rot mechanism

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Abstract: Brown-rot fungi are one of the groups of wood decay fungi, and the fungi are able to deconstruct wood cell wall efficiently with modification of lignin structure although the genes encoding lignin-degrading peroxidases were lost on the genome of the fungi. As the mechanism of brown-rot wood decay, chelator-mediated Fenton (CMF) reaction (Fe2+ + H2O2 → Fe3+ + OH¬− + ・OH) is commonly accepted. The reaction generates multitude of hydroxyl radicals that are able to rapidly attack wood cell wall components. In this mechanism, ferric iron that is stable state in natural environment in wood is reduced by phenolic compounds that are expected to be secreted by brown-rot fungi. On the other hand, lignin also possesses plentiful amount of phenolic structure, and the structure may have relationship with the iron-reducing system of CMF reaction. In the present study, iron-reducing capacities of artificially synthesized and isolated lignins and lignocellulosic materials were investigated.

Keywords: Brown-rot, Fenton reaction, Iron reduction, Electron transfer from lignin

2018-P28

白色腐朽菌ヒラタケにおける vp2, vp3 遺伝子の単独および二重破壊が木粉中のリグニン分解に及ぼす影響

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Effects of single or double disruptions of vp2 and vp3 genes on wood lignin degradation in the white-rot fungus Pleurotus ostreatus

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Abstract: White-rot fungi efficiently degrade high molecular-weight lignin in natural condition. It is generally thought that white-rot fungi secrete lignin-modifying enzymes, such as manganese peruoxidases (MnPs) and versatile peruoxidases (VPs), and they trigger oxidative degradation of wood lignin. However, it has not been examined whether these enzymes are involved in wood lignin degradation yet. In this study, we examined effects of targeted disruptions of Pleurotus ostreatus vp2 and vp3, which are predominantly expressed at the transcription level, on beechwood sawdust medium. It was shown that vp2 and vp3 disruptions do not decrease the lignin degradation quantitively. RNA-seq and quantitative RT-PCR analyses showed that transcript accumulation of mnp1, mnp2, and mnp6 increases in vp2/vp3 double disruptants. HSQC analysis suggested oxidation of G nuclear allele position increased in the double disruptants. Based on these results, it was suggested that a transcriptional regulation mechanism exists to compensate expression of mnp genes in case of a deficiency of vp genes in Pleurotus ostreatus.

Keywords: Pleurotus ostreatus, targeted gene disruption, lignin-modifying enzymes, lignin degradation, transcriptional regulation mechanism

2018-P29

白色腐朽菌ヒラタケにおける xyn10 および xyn11 遺伝子の破壊が稲わら中のリグニン分解に与える影響

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Effects of xyn10 and xyn11 disruptions on lignin degradation by the white-rot fungus Pleurotus ostreatus on rice straw medium

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Abstract: Lignin and arabinoxylan are generally linked via hydroxycinnamic acids such as ferulic acid in cell wall of grasses, which led us to examine the effects of targeted disruption of xylanase genes on lignin degradation by the white-rot fungus Pleurotus ostreatus when grown on a rice straw medium. In this study, we newly obtained some triple-gene disruptants among xyn10 (xyn10a, b, c) and xyn11 (xyn11a, b) through crossing single- and double disruptants that had been created in our previous study. We then examined the ability of each disruptant to degrade lignin and xylan present in rice straw. It was shown that ligninolytic and xylolytic activities of some triple-gene disruptants obtained in this study were lower than those of the parental strain, 20bf3. These results suggest that defects in xylan degradation way cause decrease in lignin degradation when P. ostreatus is grown on the rice straw medium.

Keywords: Pleurotus ostreatus, rice straw, xylanase, lignin degradation, gene disruption

2018-P30

白色腐朽菌ヒラタケにおけるリグニン分解不全変異株の原因変異遺伝子 gat1 及び hirA の同定

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Ligninolysis deficiency is caused by mutations in gat1 and hirA genes in the white-rot fungus Pleurotus ostreatus

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Abstract: In nature, white-rot fungi efficiently degrade high molecular-weight lignin in wood biomass. It is generally thought that the lignin degradation is triggered by fungal secreted enzymes such as manganese peroxidase (MnPs) and versatile peroxidases (VPs). However, the whole mechanisms underlying the lignin degradation remain to be elucidated. To identify new factors important in wood lignin degradation by the white-rot fungus Pleurotus ostreatus, we have introduced an efficient forward genetics approach. In this work, it was revealed that mutations in gat1 and hirA genes, which encode a putative Agaricomycete-specific DNA-binding transcription factor and a putative component of HIR complex involved in nucleosome assembly, respectively, decrease the ligninolytic activity when grown on a beechwood sawdust medium. RNA-seq analysis showed that patterns of transcript accumulation of vp/mnp genes in gat1 and hirA strains were different from those in other mutant strains defective in ligninolysis obtained in our previous studies.

Keywords: forward genetics, gene disruption, lignin degradation, manganese peroxidase, RNA-seq

2018-P31

Brevibacillus を宿主とした交雑ヤマナラシ由来酸性ペルオキシダーゼの効率的分泌生産

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Heterogeneous secretion of plant peroxidase from hybrid aspen in Brevibacillus

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Abstract: Most of plant peroxidases can oxidize coniferyl alcohol efficiently, but not sinapyl alcohol. On the other hand, a few plant peroxidases were reported to catalyze sinapyl alcohol as preferred substrate. They are suggested to have the additional active sites on the protein surface different from the heme pocket in the active site.

We tried to add the surface alternative catalytic sites of these peroxidases to PrxA3a, an anionic peroxidase of hybrid aspen, Populus X kitakamiensis, for substrate specificity modifications and for certifications of the surface amino acid residue catalyst hypothesis.

We already have succeeded heterologous expression of prxA3a in Saccharomyces cerevisiae and secretion of PrxA3a as the glycosylated form to the culture medium. To crystallize PrxA3a produced in S. cerevisiae, the deglycosylation procedure is necessary, in which the recovery yield is wrong. Then, we tried to express PrxA3a in bacteria those can't add polysaccharide chains to secretory proteins. But Escherichia coli has low ability to secret proteins and most produced secretory proteins accumulate as inclusion bodies. To gain active proteins from inclusion bodies, the procedures of denaturing and refolding are important. Brevibacillus is one genus of gram positive bacteria. It can efficiently secret active proteins as non-glycosylated forms. This unique property is considered to contribute for functional analysis and elucidation of the sugar chain role in the monolignol polymerization reaction. Secreted PrxA3a in Brevibacillus was active, and we are characterizing the secreted enzyme.

Keywords: Peroxidase; lignin; sinapyl alcohol; phytoremediation

2018-P32

Novosphingobium sp. MBES04 株のリグニン関連物質存在下におけるトランスクリプトーム解析

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Transcriptome analysis of Novosphingobium sp. MBES04 in response to lignin related compounds

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Abstract: Bacterial enzymes for β-O-4 reductive cleavage in lignin model are expected to be new tools of lignin valorization. However, high production cost for the enzymes and cofactors is a hurdle to practical processing of lignin preparations utilized as renewable materials. Biological lignin processing using bacterial cells are a potential alternative to the enzymatic processing. Novosphingobium sp. MBES04 is capable of reductive cleavage of β-O-4 linkages in some lignin breakdown materials. In order to understand metabolic pathway of this microbe for lignin processing, we here conducted transcriptomic analysis in the presence of lignin-related compounds; guaiacylglycerol-β-guaiacyl ether (GGGE), vanillin and lignin fraction extracted from hard wood (Eucalyptus globulus). We detected genes which were specifically induced in response to these compounds.

Keywords: Lignin, Novosphingobium, β-O-4 reductive cleavage, metabolic pathway, transcriptome

2018-P33

バクテリア細胞外膜におけるリグニン由来化合物取り込みメカニズムの解明

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Elucidation of the outer membrane transport of lignin-derived aromatic compounds in Sphingobium sp. SYK-6

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Abstract: Bacterial catabolic systems for low-molecular-weight aromatic compounds derived from lignin have been intensively investigated in Sphingobium sp. SYK-6. To date, over 40 catabolic enzyme genes have been isolated and functionally characterized. However, the uptake systems for these lignin-derived aromatics, specifically, their outer membrane transport remains unknown. In this study, based on the presence of a large number of homologous genes, we focused on the TonB-dependent receptor (TBDR) genes, which are generally known as outer membrane transporters of Fe3+ siderophore and vitamin B12. We found that the transcription of tbtA, one of the TBDR genes of SYK-6, was specifically induced in cells grown with 5,5'-dehydrodivanillate (DDVA). A tbtA mutant significantly decreased its capacity to grow on, convert, and uptake DDVA. Cellular localization analysis indicated that TbtA is present in the outer membrane of SYK-6. The N-terminal TonB box of TBDRs which is known to interact with the C-terminal domain of TonB is conserved in TbtA. Introduction of mutations into the TonB box of TbtA significantly affected the growth of SYK-6 on DDVA, DDVA conversion, and DDVA uptake. Based on these observations, we concluded that TbtA plays an essential role in the DDVA uptake across the outer membrane.

Keywords: Gram-negative bacteria, outer membrane transporter, TonB, biphenyl

2018-P34

Sphingobium sp. SYK-6 株におけるβ-1 型リグニン由来化合物の立体選択的な代謝システム

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Stereoselective catabolism of β-1 type lignin-derived aromatic isomersin Sphingobium sp. strain SYK-6

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Abstract: Sphingobium sp. strain SYK-6 is able to utilize various lignin-derived biaryls as the sole source of carbon and energy. A β–←1 type biaryl, 1,2-bis(4-hydroxy-3-methoxyphenyl)-propane-1,3-diol (HMPPD) consists of two diastereomers, threo and erythro, each of which has enantiomers (threo, HMPPD I and II; erythro, HMPPD III and IV). In SYK-6 cells, HMPPD I and II (threo form) are initially oxidized at Cα position to produce HMPPD-keto I and II, respectively. The Cα-dehydrogenase genes (ligD, ligL, and ligN) responsible for the catabolism of β-O-4 type biaryls were suggested to be involved in the oxidation of HMPPD I and II. In this study, we examined the role of Cα-dehydrogenases in the catabolism of HMPPD, and the catabolic pathway of HMPPD was partially determined. Among seven Cα-dehydrogenases, LigD, LigO, and SLG_12640 converted HMPPD I into HMPPD-keto I, while LigL and LigN transformed HMPPD II into HMPPD-keto II. Characterization of mutants of Cα-dehydrogenase genes showed that multiple genes (ligD, ligO, SLG_12640) are involved in the oxidation of HMPPD I while ligL has a predominant role in HMPPD II oxidation. Interestingly, SLG_12640 exhibited an ability to reduce HMPPD-keto II into HMPPD IV in the presence of NADPH. Furthermore, an SYK-6 cell extract was able to degrade HMPPD IV via vanillin without passing through HMPPD-keto as an intermediate. These results suggest that the conversion of threo-HMPPD to erythro-HMPPD through oxidation of HMPPD and reduction of the resultant HMPPD-keto is essential to degrade threo-HMPPD.

Keywords: bacteria, diarylpropane, C□-dehydrogenase□ biodegradation

2018-P35

Sphingobium sp. SYK-6 株におけるリグニン・ビフェニル化合物代謝系遺伝子群の転写制御システム

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Transcriptional regulation of the catabolic genes of a lignin-derived biphenyl compound in Sphingobium sp. strain SYK-6

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Abstract: Sphingobium sp. strain SYK-6 is a bacterium which is able to degrade various lignin-derived biaryls and monoaryls. The SYK-6 catabolic system is useful in converting these lignin-derived aromatics into value-added chemicals. To date, although a number of genes involved in the catabolism of lignin-derived biaryls including 5,5’-dehydrodivanillate (DDVA) have been identified and characterized, their transcriptional regulations remain largely unknown. In the SYK-6 genome, the genes responsible for the DDVA catabolism such as the transporter genes (tbtA and ddvK) and the catabolic enzyme genes (ligZ, ligY, and ligXa) form a gene cluster. These genes appeared to be regulated by ddvR, which encodes a MarR-type transcriptional regulator and located just upstream of ligXa. In this study, we investigated the transcriptional regulation of the DDVA catabolic genes. RT-PCR analysis showed that the DDVA catabolic gene cluster consists of three operons: the ligXa operon, the ddvR operon, and the tbtA operon containing tbtA, ddvK, ligZ, and ligY. qRT-PCR analysis using SYK-6 cells and ddvR mutant cells revealed that the transcriptions of the ligXa and tbtA operons were negatively regulated by DdvR. Electrophoretic mobility shift assay demonstrated that DdvR bound to the promoter regions of ligXa and tbtA, and DDVA functioned as an effector molecule of DdvR. In addition, the inverted repeat sequences found on the promoter regions of the ligXa and tbtA operons played an important role in the DNA binding of DdvR.

Keywords: 5-5 linkage, biphenyl, bacteria, catabolism, transcriptional regulation

2018-P36

Sphingobium sp. SYK-6 株におけるリグニン由来芳香族化合物の内膜 transporter の探索

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Exploration of the genes responsible for inner membrane transport of lignin-derived aromatic compounds in Sphingobium sp. SYK-6

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Abstract: Various enzyme genes necessary for the catabolism of lignin-derived aromatic compounds have been identified and characterized in Sphingobium sp. strain SYK-6. However, little is known about the bacterial uptake of lignin-derived aromatic compounds. The transport of aromatic acids is known to be mediated by the aromatic acid/H+ symporter (AAHS) family, one of the major facilitator superfamily transporters. In the SYK-6 genome, there are 16 putative AAHS genes, and one of these genes pcaK was found to encode a major protocatechuate transporter which has a capacity to uptake vanillate. In this study, in order to clarify whether the 16 putative AAHS genes of SYK-6 are involved in the uptake of lignin-derived aromatic compounds, mutants of all the AAHS genes and multiple mutants of seven AAHS genes with pcaK were created. Analysis of these mutants suggest that PcaK partially participates in the uptake of vanillate, syringate, and 4-hydroxybenzoate. However, the contribution of other AAHS genes to the uptake of these compounds appears to be minimal.

Keywords: bacteria, transporter , proton motive force, monomer

2018-P37

イネの GUX, XAT － RNAi 抑制株の作成と細胞壁構成成分の解析

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Making of GUX, XAT – RNAi Transformants of Rice and Analysis of Components of Plant Cell Wall

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Abstract: In our previous research, we produced transformants, which repressed the gene related to hemicellulose synthesis, and analyzed their gene expression and plant cell wall components to understand the function of hemicellulose in plant cell wall. Then, we found that both hemicellulose and lignin synthesis related genes were repressed at the same time in transformants, and this result suggested that hemcellulose and lignin biosynthesis are closely related in plant cell wall synthesis.

To elucidate this relationship in detail, we selected two genes, gluclonic acid transferase（GUX）and xylan arabinose transferase (XAT), and produced each gene knockdown-transformant (T0). T0 stocks had distorted or curved leaves character. On this research, we will report the content of sugar (glucose, xylose, and arabinose), ferulic acid, and lignin of cell wall of the transformant.

Keywords: gluclonic acid transferase（GUX）, xylan arabinose transferase (XAT), RNAi, hemicellulose, lignin

2018-P38

ヒノキ圧縮あて材細胞壁においてラッカーゼのp-クマリルアルコール取込み能力を可視化する

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Visualization of p-coumaryl alcohol incorporation by laccase at the compression wood cell walls in Japanese cypress.

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Abstract: Compression wood lignin includes p-hydroxyphenyl (H) unit, and it is believed that this unit is accumulated in the “S2L” [1], which is highly lignified region localized in the outer portion of S2 layer. In Japanese cypress (Chamaecyparis obtusa), a compression-wood-specific laccase (CoLac1) is localized in S2L [2], suggesting this enzyme may selectively oxidize H unit precursor, p-coumaryl alcohol. In this study, we visualized incorporation abilities of p-coumaryl and coniferyl alcohols at the lignifying cell walls using fluorescently-labeled monolignols [3]. In addition, we compared these results with those obtained in the supply of H2O2, to examine whether laccase or peroxidase is the main enzyme for monolignol polymerization. When the labeled coniferyl alcohol was fed to differentiating compression wood section in the removal of H2O2, the fluorescence signal was high at lignifying S1 and inner portion of S2, but low at S2L. While the fluorescence signal of the labeled p-coumaryl alcohol was high at lignifying S2L, but low at the other layers. Moreover, the labeled p-coumaryl alcohol was hardly incorporated into the normal wood cell walls during secondary wall formation. These results suggest accumulation of H unit may be caused by a p-coumaryl-alcohol-specific laccase expressed during S2L formation. Besides, the incorporation of these monolignols in compression and normal wood cell walls, were not enhanced by supply of H2O2 while reduced by conversion of dissolved O2 to H2O2. Therefore, in Japanese cypress, not peroxidase but laccase seems to be mainly responsible for lignification of the secondary wall.

Keywords: reaction wood, secondary cell wall , oxidative polymerization, guaiacyl unit

2018-P39

Altered lignin structures and improved cell wall digestibility of rice mutants deficient in tricin biosynthesis genes

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Abstract: Many grass species naturally incorporate flavonoid tricin into cell wall lignins. However, how such lignin-integrated tricin functions in planta and also how it affects the usability of grass biomass remain largely unknown. To address these issues, we isolated tricin-truncated rice mutants and analyzed their cell walls with emphasis on lignin structure and cell wall digestibility. Through chemical, histochemical and 2D NMR analyses, we demonstrated that rice mutants deficient in OsFNSII and OsCAldOMT1 comprised lignins largely depleted in tricin units. In addition, the osfnsII mutant appeared to heterologously incorporate naringenin as a novel lignin monomer. On the other hand, oscaldomt1 mutant was additionally depleted in syringyl lignin units, suggesting that OsCAldOMT1 is a bifunctional OMT involved in both the tricin and syringyl lignin biosynthetic pathways. These two mutants were further shown to display improved cell wall digestibility.
Keywords: Enzymatic saccharification, Flavone synthase II, Poaceae, 5-Hydroxyconiferaldehyde O-methyltransferase, Nuclear magnetic resonance

2018-P40

Sphingobium sp. SYK-6 株由来 Cα-dehydrogenase とマウス由来 Cx43 を共発現する組換えポプラの解析

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Analysis of transgenic hybrid poplar coexpressing Cα-dehydrogenase derived from Sphingobium sp. strain SYK-6 and mouse Cx43

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Abstract: As global warming becomes a problem, plant biomass having carbon neutral characteristic attracts attention as resources with less environmental burden. Plant biomass is a raw material such as bioethanol, but a lot of cost is required to remove lignin for the production. Therefore, it aims to reduce cost of plant biomass processing by improving degradability and separability of lignin by changing its structure by genetic engineering. Bacterial strain Sphingobium sp. SYK-6 which can utilize lignin-derived aromatic compounds as a carbon source have LigD, an enzyme involved in the degradation of a dimeric compound containing a β-O-4 type bond. It oxidizes a hydroxy group at Cα position to a keto group using NAD+as a coenzyme. It is expected that β-O-4 bond with a keto group is increased by the expression and lignin degradability is enhanced under alkaline conditions. In this study, we co-expressed a mouse NAD+ transporter, connexin, in the transgenic poplar with LigD for increase of NAD+ concentration in the cell wall and analyzed its lignin structure.
Keywords: SYK-6, LigD, Cx43, poplar, genetic engineering

2018-P41

モノリグノール生合成中間体の変換酵素遺伝子を利用したリグニンエンジニアリング

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Lignin engineering using enzyme genes for the conversion of monolignol biosynthetic intermediates

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Abstract: Lignin plays various critical roles in plant such as mechanical strength whereas it is a major obstacle to the lignocellulosic biomass utilization due to its recalcitrance. Lignin engineering is a promising strategy to reduce the biomass recalcitrance. Previously, we created transgenic plants using 47 expression constructs harboring various enzyme genes, products of which convert metabolites of monolignol biosynthetic pathways, under the control of a xylem preferential promoter derived from hybrid aspen. Transgenic plants harboring genes encoding coniferaldehyde dehydrogenase (calB), feruloyl-CoA 6'-hydroxylase (F6H1), and hydroxycinnamoyl-CoA hydratase/lyase (couA) showed apparent abnormalities in Wiesner and Mäule staining patterns. In this study, we further characterized these promising transgenic plants. An irregular xylem phenotype with collapsed vessels was observed in the CouA transgenic line. Lignin content and enzymatic saccharification efficiency tended to decreased and increased (30%□60% higher than wild type) respectively in all three lines, while they showed no marked changes in the total sugar content and monosaccharide composition.

Keywords: Arabidopsis thaliana, lignin modification, glucose productivity, monolignol biosynthetic intermediate

2018-P42

Pseudomonas fluorescens AN103 株由来のヒドロキシシンナモイル CoA ヒドラターゼリアーゼ（HCHL）遺伝子を導入したポプラの解析

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Analysis of transgenic poplar harboring the hydroxycinnamoyl-CoA hydratase-lyase (HCHL) gene derived from Pseudomonas fluorescens AN103

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Abstract: Lignocellulosic biomass, which is mainly composed of cellulose, hemicellulose, lignin. It is a carbon-positive, renewable, and sustainable resource, representing an ideal alternative to fossil resources. However, the use of lignocellulosic biomass is restricted by lignin due to its intertwined structural properties. Generally, lignin limits enzymatic accessibility and reduces hydrolysis efficiency of lignocellulose. It is biosynthesized under an unique pathway with various enzymes and phenolic lignin monomers are exported from cytoplasm to cell wall. Random oxidative polymerization of the monomers occurs in the cell wall. In this study, we produced and analyzed several transgenic poplars harboring the gene encoding the hydroxycinnamoyl-CoA hydratase-lyase (HCHL) for depletion of the intermediate of hydroxycinnamoyl-CoA in the lignin biosynthetic pathway. Resultant transgenic plants exhibited abnormal growth with brown-colored wood. We characterized their lignin contents, distribution, and monomeric compositions as well as the digestibility of the cell wall.

Keywords: chain shortening enzyme, lignin recalcitrance, transgenic plant

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Parvibaclum lavametivorans DS-1 株由来の PlDBR 遺伝子を導入した組換えポプラの解析

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Analysis of transgenic poplar transformed with PlDBR derived from Parvibaclum lavametivorans DS-1

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Abstract: The bond formed through the carbon of β-position is important for determine the chemical and physical properties of lignin. Double bond reductase (DBR) is an enzyme that catalyzes the reaction of reducing the double bond of the side chain of coniferyl aldehyde (CALD) which is a precursor of monolignol. In this study, we focused on a DBR which was derived from Parvibaclum lavametivorans DS-1(PlDBR). In order to investigate the impact of PlDBR expression to the structural changes of lignin in transgenic plants. We had surveyed the lignin content and syringyl/guaiacyl (S/G) ratios of lignin in transgenic poplar.

Keywords: PlDBR, poplar, structural changes, transgenic plant

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二次壁肥厚を促進するイネ転写因子 OsNST2 を過剰発現する CAD 発現抑制ポプラの解析

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Promoting secondary wall deposition by overexpressing the rice transcription factor OsNST2 in CAD-downregulated transgenic poplar

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Abstract: It is well known that, NAC Secondary wall Thickening factors (NST) could effectively enhance the secondary cell wall formation in plant. Overexpression of OsNST2 which is a rice ortholog gene of Arabidopsis NST in nst1 nst3 double mutant of Arabidopsis under the control of NST3 promoter leads to an increase in amount of secondary wall [1]. On the other hand, downregulation of cinnamyl alcohol dehydrogenase (CAD) expression in both Arabidopsis and poplar were effective in enhancing the saccharification yield [2][3]. Therefore, in this study, we introduced the NST3promoter::OsNST2 construct into CAD-downregulated poplar for increasing the deposition of secondary cell wall with higher saccharification efficiency. Weights of fresh and dry woods prepared from transgenic stems, cell wall width of fibers, lignin content and composition of the woods as well as enzymatic digestibility of cell wall residues were analyzed.

Keywords: Transcription factor OsNST2, Secondary cell wall, Lignin