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Mechanochemical Reactions of the Trimeric Lignin Model Compound Composed of β -Aryl Ether and β' -Aryl Ether

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Mechanochemical reactions of a trimeric lignin model compound (I) composed of β -aryl ether and β' -aryl ether were investigated and compared with these of dimeric lignin model compounds (II) and (III). Trimer (I) suffered from heavier mechanochemical conversions and formed higher numbers of degradation and condensation products than the dimers. Thirteen compounds were separated from the reaction mixtures of (I) and identified. They included vanillin **2**, veratrylglycerol- β -syringaldehyde ether **4**, syringaldehyde **8**, 3, 5-dimethoxyl-*p*-benzoquinone **9**, ketones **10** and **11** which are important leucochromophores and chromophores responsible for light-induced discoloration of bleached high-yield mechanical pulps. Homolytic cleavages of $C\alpha-C\beta$ and $C\alpha'-C\beta'$ bonds in the trimer formed two pairs of radical intermediates. The radicals recombined each other and reacted with $\cdot O_2H$, $\cdot OH$ and $\cdot H$ to give compounds **1** to **9** and unidentified condensation products. The dehydrogenation at $C\alpha'$ of Trimer (I) produced the ketone **10** which underwent further conversions to form compounds **11** to **13**.

INTRODUCTION

Previous studies on the mechanochemistry of dimeric lignin model compounds show that the various compounds including leucochromophores and chromophores formed during the mechanical treatments of the models in a ceramic ball mill (CBM), a vibration ball mill (VBM) or a laboratory refiner. The leucochromophores and chromophores were coniferylaldehyde methyl ether produced from coniferylalcohol methyl ether (Lee *et al.*, 1988), *p*-carbonyl phenols from veratrylglycerol- β -vanillin ether (Lee and Sumimoto, 1990), stilbenes with a α -carbonyl group from phenylcumarane (Lee *et al.*, 1990), stilbenes and stilbenequinone from 1,2-diarylpropane-1,2-diols (Wu *et al.*, 1991), and 3,5-dimethoxyl-*p*-hydroquinone and 3,5-dimethoxyl-*p*-benzoquinone from syringaldehyde derivatives (Wu *et al.*, 1992, 1994a). The formation of these compounds was illustrated to be one of main causes for light-induced discoloration of bleached high-yields mechanical pulps (Lee and Sumimoto, 1991; Wu *et al.*, 1994b). The mechanochemical conversions from the model compounds to the reaction products were proved to proceed mainly via radical mechanisms (Wu *et al.*, 1994c, 1995).

Since lignin is a complex biopolymer and suffer from mechanochemical conversions much easier than model compounds which are low molecular weights (Hon, 1983, 1989), the use of trimeric lignin model compounds will be reasonable toward more complex and accurate modelling for the mechanochemical studies on lignin. In the present work, Trimer (I) was synthesized and treated in the CBM or the VBM under various conditions. The reaction mixtures were separated by the means of HPLC, and the structures and

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yields of reaction products were compared with these of compounds produced from the dimers, veratrylglycerol- β -(α '-methyl) syringyl alcohol ether (II) and veratrylglycerol- β -guaiacyl ether(III).

MATERIALS AND METHODS

Analytical procedures

¹H-NMR spectra were determined in CDCl₃ using a JNM-GX400 spectrometer (400 MHz) with tetramethylsilane as an internal standard. Mass spectra (MS) were recorded on a Shimadzu QP-1000 gas chromatography mass spectrometer operating under DI conditions (70 eV). High performance liquid chromatography (HPLC) was carried out on a JASCO TRIOTAR-II with a column of DEVELOASIL-60-3 (ϕ 20 X 250 mm) using *n*-hexane/ethyl acetate/methanol as elute solvents. Quantitative analysis was carried out on the HPLC. Veratrylaldehyde, acetates of phenylcumarane and Trimer (I) were used as standard materials for monomer, dimer and trimer, respectively.

Fig. 1. Synthetic route of trimeric lignin model compound (I).

Synthesis of Trimer (I)

Trimer (I) was synthesized according to the scheme shown in Fig. 1. Veratrylglycerol- β -syringaldehyde ether was prepared by the condensation reaction of veratrylaldehyde and syringaldehyde as described earlier (Wu and Sumimoto, 1992). Two hydroxyl groups in the ether were protected as an isopropylidene derivative with 2,2-dimethoxypropane and camphorsulfonic acid (Katayama *et al.*, 1981). Guaiacoxyl acetate methyl ester was synthesized by etherizing guaiacol with chloroacetate methyl ester (Hosoya and Nakano, 1980). Veratrylglycerol- β -syringaldehyde ether and guaiacoxyl acetate methyl ester were condensed in tetrahydrofuran (THF) solution containing lithium diisopropylamide (LDA) at -78°C to give a β -hydroxy ester derivative (Wu *et al.*, 1994a, Katayama *et al.*, 1981). The β -hydroxy ester was reduced with LiAlH₄ in THF solution and acidified with a mixture of hydrochloric acid and dioxane to yield a crude Trimer (I). The purification of (I) was carried out on a silica gel column.

Identification data of Trimer (I) (acetate): amorphous; MS (*m/z*): 728(M⁺, 1), 727(3), 630(5), 629(8), 628(62), 507(3), 475(2), 474(4), 446(12), 445(57), 435(6), 402 (3),

401(1), 353(1), 295(6), 269(2), 251(4), 235(6), 209(11), 194(2), 193(10), 183(5), 182(2), 181(5), 167(13), 165(5), 152(7), 151(100), 123(3), 107(4), 95(12), 87(4), 77(5), 65(32), 55(2), 44(10) and 43(20); ¹H-NMR (CDCl₃): 1.97-2.20(12 H, m, OAc X 4), 3.71-3.89(15H, m, OMe X 5), 4.12-4.17(2H γ ', m), 4.19-4.28(2H γ , m), 4.40-4.49(H β ', m), 4.60-4.75(H β , m), 5.91-6.00(H α ', m), 6.01-6.07(H α , m), 6.76-7.04(9 H, aromatic protons).

Procedures for the mechanical treatment of Trimer (I)

Vibration ball mill(VBM)

A 1 liter-capacity vibration ball mill (Yokohama Ltd. Co.) was used. About 200 ml of high carbon chrome steel ball (ϕ 1.25 cm) were filled in the VBM. Five ml of dichloromethane solution containing 50 mg of Trimer (I) was added to 500 mg of extractive-free linter pulp, and the solvent was removed under vacuum so that (I) was distributed evenly in the pulp. The resultant pulp and 5 ml of deionized water were transferred to the mill and treated for 1 h. The amplitude of vibration and the frequency were 3 mm and 1450 per minute, respectively.

The reaction mixtures were extracted successively with methanol, ethyl acetate and acetone. The extracts were combined, filtered, dried over Na₂SO₄ and evaporated in *vacuo*. The residue was acetylated with a mixture of acetic anhydride and pyridine, and separated with the HPLC.

In the treatment in a nitrogen atmosphere, the VBM containing the samples was placed in a dry box (Tokyo Air Engineering, Co.) and the air was replaced by N₂ three times so that the VBM was full of N₂. The subsequent procedure was the same as that described above.

When the treatment was made in the presence of 1-octanol, the addition of 0.05 ml of 1-octanol to the VBM full of nitrogen was carried out in the dry box with a microsyringe. The following mechanical treatment was made as described above.

Ceramic ball mill (CBM)

The procedures for the ceramic ball milling were the same as those of the VBM. A 1 liter ceramic ball mill (Nihon Kagaku Toki Co.) containing about 400 ml of ceramic balls with 3.5 cm average diameter was used. The milling was carried out at ambient temperature (about 25°C) under 70 revolutions per minute.

Identification of the mechanochemical reaction products

The chemical structures of reaction products **1** to **13** are shown in Figs. 3 and 4. Veratrylalcohol **1**, vanillin **2**, veratrylglycerol- β -syringaldehyde ether **4**, veratrylglycerol- β -syringylalcohol ether **5**, 2-guaiacoxyl ethanol **6**, 1-veratrylglycerol **7**, syringaldehyde **8**, 3,5-dimethoxyl-*p*-benzoquinone **9**, α -(2-methoxylphenoxy)- β -hydroxypropiosyringone **12**, and syringic acid **13** were identified by the direct comparison of melting points, MS- and ¹H-NMR spectra with values for authentic samples (Wu et al., 1992, 1994a, Nakatsubo *et al.*, 1975, 1979). Compounds **3**, **10** and **11** were identified as follows:

Compound **3** (acetate): amorphous; MS(*m/z*): 520(M⁺, 10), 435(4), 434(26), 420(9), 354(6), 331(4), 324(17), 310(2), 270(5), 269(11), 255(3), 251(8), 235(4), 226(8), 225(7), 210(11), 209(91), 198(6), 197(15), 151(20), 124(4), 109(4), 87(100), 45(50), and 43(60); ¹H-NMR(CDCl₃): 2.01-2.18(9H, m, OAc X 3), 3.72-3.81(9H, m, OMe X 3),

4.13-4.19(2H γ ', m), 4.23-4.37(2H γ , m), 4.45-4.50(H β ' , m), 4.70-4.76(H β , m), 6.01-6.04(H α ', m), 6.60-6.99(6H, aromatic protons).

Compound **10** (acetate): amorphous; MS(*m/z*):684(*M*⁺,5),642(3),548(5),510(15),476(23),475(4),420(9),350(4),331(24),310(2),296(3),295(17),269(11),254(3),251(8),224(7),209(31),198(12),197(27),181(17),167(100),154(14),139(10),123(11),109(4),107(7),91(5),77(6),45(19),and 43(25); ¹H-NMR(CDCl₃):2.01-2.16(9H, m, OAc $\times$ 3),3.84-3.95(15H, m, OMe $\times$ 5),4.13-4.19(2H γ , m), 4.20-4.31(2H γ ', m), 4.65-4.76(H β , m), 6.08-6.10(H α , m), 6.25(H β ' , t), 6.78-7.12(9H, aromatic protons).

Compound **11** (acetate): amorphous; MS(*m/z*):814(*M*⁺,1),772(6),742(10),691(3),677(15),605(17),575(4),520(2),478(45),434(12),354(7),324(9),314(60),296(4),266(15),209(9),196(6),195(13),167(100),165(10),152(12),151(30),123(4),109(2),107(9),95(14),77(12),65(7),55(3),45(20),and 43(53); ¹H-NMR(CDCl₃): 1.67-1.74(H β , m), 2.03-2.20(15H, m, OAc $\times$ 5),3.69-3.90(15H, m, OMe $\times$ 5),3.98-4.09(2H γ , m), 4.13-4.17(2H γ , m), 4.23-4.30(2H γ ', m), 4.40-4.42(H β , m), 4.75-4.78(H β ' , m), 6.03-6.05(H α , m), 6.08-6.12(H α ', m) and 6.78-7.12(9H, aromatic protons).

RESULTS AND DISCUSSION

Mechanochemical reactions of Trimer (I)

Trimer (I) was dispersed in extract-free linter pulp and treated under the conditions of CBM(air), VBM(air), VBM(N₂), and VBM(N₂, 1-octanol), respectively. As a result of the mechanical treatments, thirteen compounds were isolated from the reaction mixtures and identified. These compounds included vanillin **2**, veratrylglycerol- β -syringaldehyde

Table 1. Yields of mechanochemical reaction products from Trimer (I).

Treatments Products	CBM (air)	VBM (air)	VBM (N ₂)	VBM (N ₂ ,1-octanol)
Trimer (I)	81.3*	68.7	79.1	79.5
Compound 1	0.02	0.1	0.02	0.04
2		0.1	0.01	
3	3.2	5.1	1.0	1.0
4	3.2	4.9	0.7	
5	0.2	1.2	0.2	0.1
6	0.1	0.2	0.2	0.1
7	0.3	0.5	0.1	0.1
8	0.6	1.1	0.5	0.5
9	0.2	2.2	0.04	
10	2.4	2.9	0.8	0.1
11	1.0	1.4	0.3	
12	0.9	1.2	0.5	0.1
13	0.1	0.2	0.1	0.05
Unidentified	6.8	9.3	16.1	17.8
Totals	19.0	30.4	20.6	19.9

* weight % on starting Trimer (I).

	(I)	(II)	(III)
Molecular weight	560	406	332
Numbers of identified products	13	12	4
Combined yields of the products (weight % on starting materials)	30.4	13.1	2.5

Fig. 2. A comparison of mechanochemical reactivities of the dimeric and trimeric lignin model compounds.

ether 4, syringaldehyde 8, 3,5-dimethoxyl-*p*-benzoquinone 9, ketones 10 and 12, which were proved to be important leucochromophores and chromophores responsible for light-induced discoloration of bleached mechanical pulps (Lee and Sumimoto, 1991; Wu et al., 1994). In addition, three unidentified fractions also were separated by the HPLC from the reaction mixtures. Combined yields of the whole products obtained from the four treatments were 19.0, 30.4, 20.6 and 19.9%, respectively.

By the comparison of the compounds obtained from Trimer (I) with those from Dimers (II) and (III) treated in the VBM under air, it is found that the larger the molecular size of the model compounds was, the larger the numbers of the converted compounds were, and the higher the yields of the reaction products were. As shown in Fig. 2, only four compounds in the combined yield of 2.5% were produced from (III) having the molecular weight of 332, while thirteen compounds in the combined yield of 30.4% were formed from (I) which had the molecular weight of 560. This may be because Trimer (I) suffered from heavier mechanical stress than Dimers (II) and (III) due to its larger molecular structure.

On the other hand, much more condensation products also were obtained from the reaction mixture of the trimer as compared with these produced from the dimers. The yields of condensation products from Dimer (II) in the treatments of CBM (air) and VBM (air) were 1.0 and 1.4% (Wu *et al.*, 1994c), while the unidentified compounds of Trimer (I) were 6.8 and 9.3% under the identical conditions as shown in Table 1. The unidentified products contained mainly three fractions separated from the reaction mixtures of (I) by the HPLC. Further separation of the fractions by the HPLC operating under the different conditions showed that each of the fractions consisted of several compounds with similar chemical structures. The maximum ion peaks of MS spectra for the three fractions were 914, 990 and 995, respectively. These results of the HPLC separations and the MS spectra suggested that the fractions may be the mixtures of condensation compounds because the molecular weight of (I) was 560.

Thus the results obtained above illustrate that both degradation and condensation reactions of the lignin model compounds increased with the increase of their molecular

Fig. 3. Possible mechanochemical conversions through homolytic C α -C β cleavages of Trimer (I) induced by mechanical energy (M.E.).

weights, and suggest that lignin in wood suffers from heavy mechanochemical conversions.

Based on the chemical structures of the reaction products obtained here and on the work reported previously, main reaction pathways from (I) to the compounds are proposed as 1) generation of oxygen-containing radicals, e.g. $\cdot\text{OH}$ and $\cdot\text{O}_2\text{H}$, in the aqueous media during milling, 2) homolytic cleavages of the C α -C β and the C α' -C β' bonds in (I) and the ketone **10** to form pairs of radical intermediates, 3) dehydrogenation at C α' of (I) by $\cdot\text{OH}$ and $\cdot\text{O}_2\text{H}$ to convert α' -hydroxyl group to carbonyl group. Details for these reactions will be discussed below.

Homolytic cleavages of the C α -C β bonds in the trimer

Among the thirteen identified products, the formation of veratrylalcohol **1**, (4-ethyleneglycol) syringylglycerol- β -guaiacyl ether **3**, veratrylglycerol- β -syringaldehyde ether **4**, veratrylglycerol- β -syringylalcohol ether **5**, and 2-guaiacoxyl-1-ethanol **6** indicates that the homolytic cleavages of the C α -C β and the C α' -C β' bonds in Trimer (I) occurred during the mechanical treatments. The compounds **1** to **3** were produced via the C α -C β cleavage, and compounds **4** to **9** resulted from the C α' -C β' cleavage of (I). The possible reaction mechanisms are proposed as shown in Fig. 3.

Homolytic cleavages of the C α -C β and the C α' -C β' bonds in (I) induced by mechanical energy (M.E.) form two pairs of radicals (a), (b) and (c), (d). Radical (a) may either couple with a $\cdot\text{H}$ to produce compound **1**, or react with a $\cdot\text{OH}$ to form vanillin **2**. These reactions are the same as these of the dimers (Wu et al., 1992 and 1994c). Radical (b) and (d) also couple with a $\cdot\text{H}$ to give (4-ethyleneglycol) syringylglycerol- β -guaiacyl ether **3** and 2-guaiacoxyl-1-ethanol **6**, respectively. It is notable that considerable amounts of veratrylglycerol- β -syringaldehyde ether **4** and veratrylglycerol- β -syringalde-

Fig. 4. Possible mechanochemical conversions through the dehydrogenation reactions of Trimer (I) induced by mechanical energy (M.E.).

hyde ether **4** were formed via radical (c). Previous studies (Wu et al., 1992, 1994a) have shown that compound **4** can undergo mechanochemical conversions to form 1-veratrylglycerol **7**, syringaldehyde **8**, 3,5-dimethoxyl-*p*-benzoquinone **9** and other compounds during the millings.

The formation of compounds 4, 8 and 9 via C α '-C β ' cleavage is significant in explaining the increase of carbonyl structures in the mechanical treatments of wood lignin. Pew (1957) and Chang et al. (1975) observed that the millings of MWL (milled wood lignin) in VBMs decreased the molecular weights of the lignins and increased the contents of carbonyl groups based on IR-spectra. However, how and what kinds of carbonyl structures were generated in the lignin were unclear.

In the previous paper (Wu et al., 1994a), we reported that the mechanical treatments of Dimer (II) resulted in the conversion of α' -hydroxyl group to α' -carbonyl group through the dehydrogenation at $C\alpha$ of Dimer (II) by $\cdot OH$ and $\cdot O_2H$ which simultaneously generate in the aqueous media during millings. The present findings reveal that the formation and conversions of carbon radicals with hydroxyl groups *via* homolytic cleavage of $C\alpha-C\beta$ bonds is another route to form α -carbonyl groups in lignin during mechanical treatments.

Formation of a -carbonyl groups through the dehydrogenation at a '-carbon of Trimer (I)

As mentioned above, the dehydrogenation at Ca' of Dimer (II) is a very important pathway to form α -carbonyl structures during the mechanical treatments. Since two α -carbons are present in Trimer (I), the same mechanochemical reaction to form α -

carbonyl structures can be expected in the millings of (I). This is proved by the formation of the ketone 10, condensation compound 11, α' -(2-methoxyphenoxy)- β -hydroxypropiosyringone 12, syringic acid 13 and other compounds.

Figure 4 shows possible mechanochemical conversions from (I) to compounds 10 to 13. By the introduction of mechanical energy during the millings, Trimer (I) was dehydrogenated first to form ketone 10 possibly by co-existing $\cdot\text{OH}$ and $\cdot\text{O}_2\text{H}$. The involvement of $\cdot\text{OH}$ and $\cdot\text{O}_2\text{H}$ in the formation of compound 10 was illustrated by the results of the mechanical treatment of (I) under the atmosphere of nitrogen. When the treatment in the VBM was carried out under nitrogen, the yield of compound 10 decreased from 2.9% under air to 0.8% under nitrogen as shown in Table 1. This is because the removal of oxygen from the VBM could reduce dramatically the formation of $\cdot\text{OH}$ and $\cdot\text{O}_2\text{H}$ (Wu et al., 1995). By scavenging $\cdot\text{OH}$ and $\cdot\text{O}_2\text{H}$ with 1-octanol under nitrogen, the amount of compound 10 was decreased further to 0.1%.

Owing to the electron-withdrawing effect of α' -carbonyl group, homolytic cleavage of $\text{C}\beta$ -O bond in compound 10 occurred to give the pair of radicals (e) and (f). Radical (e) coupled either with a $\cdot\text{OH}$ to form veratrylglycerol 7 or combined with radical (b) to yield condensation compound 11. On the other hand, radical (f) may couple with a $\cdot\text{H}$ to give α' -(2-methoxyphenoxy)- β -hydroxypropiosyringone 12. Further reactions of compound 12 produced syringaldehyde 8, 3,5-dimethoxy-*p*-benzoquinone 9, syringic acid 13 and other products.

CONCLUSIONS

The mechanical treatments of the trimeric lignin model compound (I) in a ceramic ball mill (CBM) or a vibration ball mill (VBM) resulted in the formation of thirteen identified compounds in considerably high yields. The products include a number of leucochromophores and chromophores, e.g. vanillin 2, syringaldehyde 8, 3,5-dimethoxy-*p*-benzoquinone 9, ketones 10 and 12. Trimer (I) suffered from heavier mechanochemical conversions than Dimers (II) and (III).

The mechanochemical conversions from (I) to compounds 1 to 13 took place through two main pathways: 1) homolytic cleavages of the $\text{C}\alpha$ - $\text{C}\beta$ and the $\text{C}\alpha'$ - $\text{C}\beta'$ bonds in (I), and 2) dehydrogenation at α' -carbon of (I). The oxygen-containing radicals, e.g. $\cdot\text{OH}$ and $\cdot\text{O}_2\text{H}$, were generated and involved in the mechanochemical conversions during the millings.

REFERENCES

- Chang, H-m., Cowling, E.B. and Brown, W. 1975. Comparative studies on cellulytic enzyme lignin and milled wood lignin of Sweetgum and spruce. *Holzforschung*, **29**: 165-168
- Hosoya, S. and J. Nakano 1980. Reaction of α -carbonyl group in lignin during alkaline hydrogen peroxide bleaching. *Mokuzai Gakkaishi*, **26**(2): 97-101
- Hon, David N.-S. 1983. Mechanochemical reactions of lignocellulose materials. *J. Appl. Poly. Sci., Appl. Poly Symp.*, **34**: 461-487
- Hon, David N.-S. 1989. Private Letter.
- Katayama, T., F. Nakatsubo and T. Higuchi 1981. Syntheses of guaiacylglycerol- β -aryl ethers. *Mokuzai Gakkaishi*, **27**: 223-230

- Lee, D.-Y., S. Tachibana and M. Sumimoto 1988. Mechanochemical reactions of coniferyl alcohol methyl ethers. *Cellulose Chem. Tech.*, **22**(2):201-210
- Lee, D.-Y. and M. Sumimoto 1990. Mechanochemical reactions of β -O-4 lignin model compounds. *Holzforschung*, **44**: 347-350
- Lee, D.-Y., M. Matsuoka and M. Sumimoto 1990. Mechanochemical reactions of phenylcoumaran models. *Holzforschung*, **44**: 415- 418
- Lee, D.-Y. and M. Sumimoto 1991. An Intensive Chromophore in Mechanical pulps Bleached with Alkaline Hydrogen Peroxide. *Holzforschung*, **45**(Suppl.): 15-20
- Nakatsubo, F., K. Sato and T. Higuchi 1975. Syntheses of guaiacylglycerol- β -guaiacyl ether. *Holzforschung*, **29**:165-168
- Nakatsubo, F. and T. Higuchi 1979. Syntheses of phenylcoumaran. *Mokuzai Gakkaishi*, **25**: 735-742
- Pew, J. C. 1957. Properties of powered wood and isolation of lignin by cellulytic **enzyme**. *Tappi*, **40**: 553-558
- Wu, Z.-h., M. Matsuoka, D.-Y. and M. Sumimoto 1991. Mechanochemical reactions of β -1 lignin model compounds. *Mokuzai Gakkaishi*, **37**: 164-171
- Wu, Z.-h. and M. Sumimoto 1992. Mechanochemical conversions of veratrylglycerol- β -syringaldehyde ether. *Mokuzai Gakkaishi*, **38**: 277-284
- Wu, Z.-h., M. Sumimoto and H. Tanaka. 1994a. mechanochemical reactions of veratrylglycerol- β -(α' -methyl)syringyl alcohol ether. *Acta Chimica Hungarica-Model in Chem.*, **131**(5):571-580
- Wu, Z.-h., M. Sumimoto and H. Tanaka. 1994b. A novel approach to improve brightness stability of H₂O₂-bleached high-yield pulps by addition of radical scavengers to the pulping process. *Holzforschung*, **48**: 400-404
- Wu, Z.-h., M. Sumimoto and H. Tanaka. 1994c. Factors influencing mechanochemical reactions of veratrylglycerol- β -syringaldehyde ether. *Holzforschung*, **48**: 395-399
- Wu, Z.-h., M. Sumimoto and H. Tanaka. 1995. Generation of oxygen-containing radicals in the aqueous media of the mechanical pulping. *J. Wood. Chem. Tech.*, **15**(1): 27-42