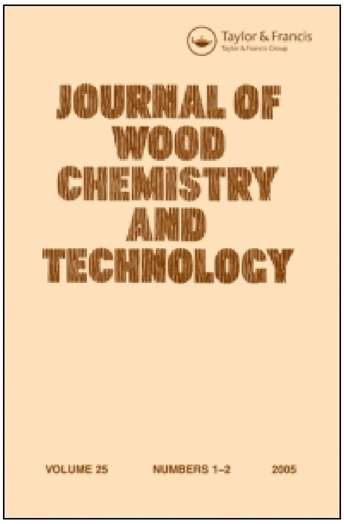

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MECHANOCHEMISTRY OF SYRINGYLGLYCEROL-β-GUAIACYL ETHER AND ITS SIMILARITY TO THE CONVENTIONAL BLEACHING OF MECHANICAL PULPS.*

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ABSTRACT

Syringylalcohol (1), α-methyl syringylalcohol (2), 3,4,5-trimethoxyphenyl methylcarbinol (3) were dispersed onto filter paper pulp or linter pulp, and treated, respectively, with a ceramic ball mill (CBM) or a vibration ball mill (VBM-1 or -2) under air for 1h. Mechanical treatment of VBM-2, having the more rigid surface of linter pulp, furnished the *p*-carbonylphenols (5), (6), and 3,5-dimethoxy-*p*-benzoquinone (7). Mechanical treatments of syringylglycerol-β-guaiacyl ether (4) with CBM, VBM, and a laboratory refiner provided α-(2-methoxyphenoxy)-β-hydroxypropiosyringone (8) in the highest yield and a less yield of *p*-quinone derivative (7) and others as shown in TABLE 2 and FIGURE 3. When treated the resultant mixture with alkaline H_2O_2, the chromophore (Ⅲ) can be decomposed, but remarkable amounts of the leucochromophre (Ⅳ) are produced as shown in FIGURE 4.

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*This article is a Part XⅡ of a serial study:Mechanochemistry of Lignin.

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INTRODUCTION

Based on ultraviolet spectroscopy, Pew[1] suggested that *para*-carbonyl phenols and coniferyl aldehyde groups were produced during the milling of milled wood lignin (MWL) with a vibratory ball mill (VBM). In 1975, Chang, Cowling, and Brown[2] observed that grinding cellulolitic enzyme lignin (CEL) with a VBM increased α-carbonyl and phenolic hydroxyl groups in the lignin.

It was mentioned later by Hosoya and Nakano[3] and Nonni and Dence[4] that the treatment of α-(2-methoxyphenoxy)-β-hydroxypropioguaiacone with alkaline H_2O_2 formed relatively high amounts of the corresponding *p*-hydroquinone, which was oxidized gradually to the corresponding *p*-quinone under air even at the room temperature. More recently, Cole and Sarkanen[5] found that the color reversion of the bleached mechanical pulp could be effectively restrained by addition of a thiol derivative.

Lee and Sumimoto[6] reported that the treatment of veratrylglycerol-β-vanillin ether with a ceramic ball mill (CBM) for 1h firstly induced the cleavage of a Cα-Cβ bond to give 5.5 % of veratryl alcohol, 0.8 % of vanillin-ethylene glycol ether, 18.8 % of vanillin, and others. Whole reactions occurred were well-explained only when assumed the presence of $\cdot$H and $\cdot$OH radicals in the reaction media. When phenylcoumaran derivatives[7] having a *p*-carbonyl group in the B-ring were treated with a CBM, VBM or a laboratory refiner, considerable amounts of stilbenes having a *p*-carbonyl phenol structure on the B-ring were also obtained. Based on the results mentioned above, Lee and Sumimoto[8] suggested that a major cause of the intensive color reversion of bleached mechanical pulps should be ascribed to the occurrence of 5-substituted *p*-hydroquinones.

Itoh and others[9] recently found that the mechanical treatment of both syringaldehyde and acetosyringone with VBM produced 3,5-dimethoxy-p-benzoquinone. Recently Wu and Sumimoto[10] reported that treatment of veratryl glycerol-β-syringaldehyde ether with a laboratory refiner instantaneously caused the significant Cα-Cβ splitting reaction to give 5.1 % of veratrylalcohol, 0.7 % of syringaldehyde-ethyleneglycol ether, 1.4 % of vanillin, 5.8 % of syringaldehyde, 1.5 % of 3,5-dimethoxy-*p*-hydroquinone, 2.3 % of 3,5-dimethoxy-*p*-

benzoquinone, and others. Whole reactions proceeded in the laboratory refiner can be fully understood only when assumed the generation of high concentration of • H, • OH, and • O_2H radicals in the aqueous media. Further confirmation of the generation of ultrasonic waves will be published in the forthcomming paper.

In the previous report[9], the mechanochemistry of syringaldehyde, acetosyringone, and α-(2-methoxyphenoxy)-β-hydroxypropiosyringone was investigated to study the reaction mechanism. Therefore, the present report deals with the mechanochemistry of syringylalcohol (1), α-methyl syringylalcohol (2), 3,4,5-trimethoxyphenyl methylcarbinol (3), and syringylglycerol-β-guaiacyl ether (4).

EXPERIMENTAL

Separation and quantitative analyses of mechanochemical conversion products from the model compounds (1) to (4) were accomplished by preparative thin layer chromatography (TLC) and high-pressure liquid chromatography (HPLC). Preparative TLC was performed on a glass sheet with a silica-gel (kieselgel 60 PF_{254}) layer of 1.5 mm thickness. HPLC was performed on a Jasco Trirotar- II using a Chemcopack column (20× 270 mm).

Identification of the products was made by comparison of melting points (mp) and mixed mps with authentic samples. In addition, ultraviolet (UV), direct inlet mass (DI-MS) and proton nuclear magnetic resonance (^{1}H-NMR) spectra were compared to authentic samples. UV spectra were recorded on a Hitachi model 200-20 spectrophotometer using MeOH as a solvent. DI-MS were recorded on a Shimadzu QP-1000 mass spectrometer. ^{1}H-NMR spectra were measured in $CDCl_3$ with a JNM-GX 400 spectrometer with Me_4Si as the internal standard.

Preparation of syringylalcohol (1), α-methyl syringylalcohol (2), and 3,4,5-trimethoxyphenyl methylcarbinol (3).

To a mixture of 0.6 ml of benzene and 1 ml of water containing either 1 mmol of the acetate of syringaldehyde (5) or that of acetosyringone (6), 0.6 mmols of potassium borohydride and 0.05 mmols of a phase-transfer catalyst (PTC), N-dodecyl-N-methylephedrium bromide[11] were added and agitated at room temperature for 1 h. In another experiment, a mixture of 0.6 ml of benzene and 1 ml of water containing 1 mmol of 3,4,5-trimethoxy acetophenone, acetosyringone, 0.6 mmols of potassium borohydride and 0.05 mmols of PTC[11] as mentioned above were added and agitated at room temperature for 1 h. After acidification to pH 3 with 10 % aqueous HCl, each reaction mixture was extracted four times with 2 ml of benzene. The benzene solution was washed with 1 ml of brine and dried over sodium sulfate and evaporated *in vacuo*. To each solution of the resulting reaction mixture in MeOH , 0.2 N aqueous KOH was added at 0 ℃ under N_2. After stirring for 15 min, the solution was acidified with 2 N aqueous HCl and extracted with dichloromethane. The extract was washed with brine and dried over anhydrous Na_2SO_4. After removal of the solvent *in vacuo*, the crude syrup was chromatographed on silica-gel column (Wakogel C-200) with ethyl acetate/*n*-hexane (1:1) to give 153 mg of syringylalcohol 1, 171 mg of α-methyl syringylalcohol 2, and 166 mg of 3,4,5-trimethoxyphenyl methylcarbinol (3).

Syringylalcohol (1) : mp 124-125 ℃ ; DI-MS (70 eV) *m/z* (intensity, %) : 184 (100, M^+), 155 (12.7), 123 (5.0). α-Methyl syringylalcohol (2) : mp 93-96 ℃ ; DI-MS (70 eV) *m/z* (%) : 198 (62.1, M^+), 183 (58.5), 155 (33.9), 123 (67.6), 95 (37.3), 43 (100). 3,4,5-trimethoxyphenyl methylcarbinol (3) : DI-MS (70 eV) *m/z* (%) : 212 (78.1, M^+), 198 (61.5), 170 (75.4), 155 (41.8), 138 (53.5), 43 (100).

Treatment of syringylalcohol (1), α-methyl syringylalcohol (2),and 3,4,5-trimethoxyphenyl methylcarbinol (3) with CBM and VBM-1, and -2, respectively.

One hundred mg of syringylalcohol (1) and α-methyl syringylalcohol (2), each dissolved in 2 ml of acetone were dispersed onto 0.2 g of filter paper pulp and the solvent was removed *in vacuo*. The resulting filter paper pulp and 2 ml of water were put into either a CBM (Nihon Kagaku Togyou Company, 1 liter) or VBM (designated VBM-1) (SM-60, Yokohama Ind. Ltd. Co.), and treated under air for 1h.

In another experiment, 100 mg each of two alcohols (1) and (2) were dispersed onto 0.2 g of linter pulp which was treated with VBM under air for 1 h (designated VBM-2). As a comparative experiment, 100 mg of 3,4,5-trimethoxyphenyl methylcarbinol (3) was dispersed onto 0.2 g of filter paper pulp which was treated with VBM-1 under air for 1 h. The reaction mixtures in CBM or VBM were extracted twice with 100 ml of methanol followed by two extraction with 100 ml of ethyl acetate. The combined extracts were filtered, dried over anhydrous sodium sulphate, and evaporated *in vacuo*. The residues from syringylalcohol (1) were 90.6 mg (CBM), 93.3 mg (VBM-1), and 95.6 mg (VBM-2). The residues from α-methyl syringylalcohol (2) were 89.1 mg (CBM), 91.5 mg (VBM-1), and 92.8 mg (VBM-2). The residues from 3,4,5-trimethoxyphenyl methylcarbinol (3) were 90.4 mg (CBM), 93.6 mg (VBM-1), and 93.8 mg (VBM-2). The resulting mixtures mentioned above were separated by HPLC (methanol:dichloromethane=1:9).

From the residues in CBM, VBM-1, and VBM-2, 86 mg, 80 mg, and 75 mg of syringylalcohol (1) were recovered, respectively, in addition to 1.3 mg, 2.1 mg, and 2.5 mg of pale yellow crystals. These crystals had a mp of 108-110℃; DI-MS (70eV) *m/z* (%): 182(15.9, M^+), 181(18.4), 151(100), and 91(20.7). Comparison of mp, mixed mp, and DI-MS confirmed its identity as syringaldehyde (5). Another product from syringylalcohol (1) with CBM, VBM-1, and VBM-2 was present in trace amounts, 0.4 mg, and 0.5 mg of yellow crystals, respectively, having mp 108-110℃; DI-MS (70eV) *m/z* (%): 168(19.3, M^+), 80(22.6), 69(100), 53(31.6). Mp and mixed mp as well as comparison of DI-MS confirmed its identify as 3,5-dimethoxy-*p*-benzoquinone (7).

Treatment of 100 mg of α-methyl syringylalcohol (2) with CBM, VBM-1, and VBM-2, yielded 87 mg, 85 mg, and 78 mg of the starting materials, respectively, but also furnished 0.6 mg, 1.4 mg, and 1.7 mg of white needles, having mp 125-128℃; DI-MS (70eV) *m/z* (%): 196(25.3, M^+), 181(100), 165(28.1), 106(18.3). Mp and mixed mp, and comparison of DI-MS confirmed its identity as acetosyringone (6). Another product from the same treatment with CBM, VBM-1, and VBM-2 furnished a trace, 0.2 mg, and 0.3 mg of yellow crystals, respectively, which was identified as 3,5-dimethoxy-p-benzoquinone (7) through comparisons of DI-MS, mp and mixed mps.

Treatment of 100 mg of 3,4,5-trimethoxyphenyl methylcarbinol (3) with CBM, VBM-1, and VBM-2, yielded 90 mg, 88 mg and 81 mg of the starting materials, but furnished 0 mg, 0.2 mg, and 0.3 mg of white needles, having mp 126-127℃ ; DI-MS (70eV) *m/z* (%): 196(28.6, M^+), 181(100), 165(30.8), 106(20.4). Mp and mixed mp and comparison of DI-MS confirmed its identity as acetosyringone (6).

Synthesis of syringylglycerol-β-guaiasyl ether (4).

According to the method of Nakatsubo and others[12], syringylglycerol-β-guaiasyl ether (4) was synthesized in the total yield of 88 % from syringaldehyde. DI-MS (70 eV) *m/z* (%) : 473 (1.1 M^+), 431 (1.3), 389 (2.1), 347 (1.5); ^{1}H-NMR (400 MHz, $CDCl_3$) (acetate), δ (ppm) : 2.31 (3 H, s, -OAc), 3.76 (6 H, s, syringyl aromatic-OMe), 3.81 (3 H, s, guaiacyl aromatic-OMe), 4.08 (2 H, m, CH_2), 6.86 (4 H, m, guaiacyl aromatic), 6.97 (2 H, d, J = 1.5 Hz, syringyl aromatic).

Mechanical treatment of compound (4).

Treatment of compound (4) under air with either CBM or VBM-1.

One hundred mg of compound (4) dissolved in 2 ml of dichloromethane was dispersed onto 0.1 g of filter paper pulp, and the solvent was removed *in vacuo*. One ml of water was added to the pulp and treated with either CBM or VBM under air for 1h. The reaction mixtures in CBM or VBM was extracted twice with 100 ml of methanol followed by two extractions with 100 ml of ethyl acetate. The combined extracts were filtered, dried over anhydrous sodium sulphate, and evaporated *in vacuo*. The residues from compound (4) were 90.5 mg (CBM), 81.8 mg (VBM). The starting material (4), 58.3 mg (CBM) and 50.5 mg (VBM), respectively, were recovered from the reaction mixture by preparative TLC (benzene:ethyl acetate:formic acid=15:4:1), and the resulting products were separated and purified further by HPLC (methanol:dichloromethane=1:19). The yields of the identified compounds are shown in TABLE 2.

Treatment of compound (4) with a laboratory refiner.

As mentioned in the previous paper[9], we named the pulps which passed through only the first TMP refiner at an elevated temperature in a mill as "1R-pulps". The "1R-pulps" were extracted repeatedly with an alcohol-benzene mixture (1:2) followed by methanol to prepare extractives-free "1R-pulps". Five hundred mg of compound (4) dissolved in 5 ml of dichloromethane were dispersed in 50 g of extractives-free "1R-pulps", and then the solvent was removed under stirring *in vacuo*. The resulting pulps were fed into an open type KRK-refiner for the second refining with clearance of 0.1 mm and pulp consistency of 10 %, to produce 37 g of "2R-pulps" with CSF (Canadian Standard of Freeness) of about 200 ml. After filtration, "2R-pulps" were extracted with 300 ml of alcohol-benzene mixture (1:2) at 60℃ for 6h. The exhausted water was also extracted three times with 100 ml of ethyl acetate. Both extracts were combined and dried over sodium sulfate and concentrated *in vacuo*. For identification of the reaction products, 272 mg of the reaction mixture were recovered and separated by preparative TLC followed by HPLC (methanol:dichloromethane=1:9) to give 225 mg of the starting material. The yields of the identified compounds are shown in TABLE 2 and FIGURE 3. For comparison, a second refining of the extractives-free "1R-pulps" was also made under the same conditions as mentioned above. However, no identifiable compound was obtained.

Treatment of compound (4) under N_2 with VBM.

One hundred mg of lignin model compound (4) dissolved in 5 ml of dichloromethane was added to 0.1 g of filter paper pulp, and the solvent was removed *in vacuo*. One ml of water was added to the resulting pulp in the VBM and the air in the VBM was replaced three times by nitrogen in a Glove Box (Tokyo Air Engineering Inc.). The sample was then treated in the usual manner for 1h. From the resulting reaction mixture, 81.6 mg of the starting material (4) was recovered by preparative TLC and the residue was separated by HPLC. Identification of four conversion products including (7), (8), (9), and (10), was made by comparisons of mp and mixed mp, DI-MS and ^{1}H-NMR spectra, as shown in the following section. However, identification of the two compounds (11) and (12) were made only using TLC. Yields of the identified products are shown in Table 2.

Identification of mechanochemical conversion products.

The chemical structures for six conversion products (7)~(12), shown in FIGURE 3, from the starting materials were identified through comparison of mp and mixed mp, DI-MS and ^{1}H-NMR spectra. The yields of reaction products were determined by preparative TLC followed by HPLC and are shown in weight percent in Table 2.

α-(2-Methoxyphenoxy)-β-hydroxypropiosyringone (8) : mp 93-94 ℃ ; DI-MS (70 eV) m/z (%) : 318 (20.5 M$^+$), 181 (100), 167 (10.5), 77 (11.2); ^{1}H-NMR(400 MHz, CDCl$_3$) (acetate), δ (ppm):2.31 (3 H, s, -OAc), 3.76 (6 H, s, syringyl aromatic-OMe), 3.81 (3 H, s, guaiacyl aromatic-OMe), 4.08 (2 H, m, CH$_2$), 6.86 (4 H, m, guaiacyl aromatic), 6.97 (2 H, d, J = 1.5 Hz, syringyl aromatic).

α-(2-Methoxyphenoxy)-β-hydroxypropionic acid (9) : 81-83 ℃ ; DI-MS (70 eV) m/z (%) : 212 (20.1 M$^+$), 182 (100), 165 (5.1), 137 (10.3) ; ^{1}H-NMR (400 MHz, CDCl$_3$) (acetate), δ (ppm) : 3.85 (3 H, s, -OMe), 3.98 (2 H, d, J = 1.8 Hz, CH$_2$), 4.61 (H, m, CH), 6.95 (4 H, m, aromatic protons).

(2-Methoxyphenoxy)-1,2-dihydroxy ethane (10) : 130-133 ℃ ; DI-MS (70 eV) m/z (%) : 268 (10.2, M$^+$), 225 (11.1), 182 (100), 166 (6.3), 152 (10.5) ; ^{1}H-NMR (400 MHz, CDCl$_3$) (acetate), δ (ppm) : 2.23 (6 H, s, -OAc), 3.86 (3 H, s, -OMe), 4.05 (2 H, t, J = 1.1 Hz, CH$_2$), 4.81 (H, m, CH), 6.99 (4 H, m, aromatic protons).

Syringic acid (11) : 105-108 ℃ ; DI-MS (70 eV) m/z (%) : 198 (100, M$^+$), 181 (19.3), 154 (11.8), ; ^{1}H-NMR (400 MHz, CDCl$_3$) (acetate), δ (ppm) : 3.81 (6 H, s, -OMe), 6.88 (2 H, d, J = 1.3 Hz, aromatic protons).

2-(2-Methoxyphenoxy)glycollic acid (12) : 75-77 ℃ ; DI-MS (70 eV) m/z (%) : 182 (100, M$^+$), 165 (10.8), 137 (12.8), 107 (21.3) ;

^{1}H-NMR (400 MHz, $CDCl_3$) (acetate), δ (ppm) : 3.77 (3 H, s, -OMe), 3.85 (2 H, s, CH_2), 6.88 (4 H, m, aromatic protons).

RESULTS AND DISCUSSION

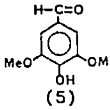
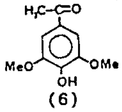
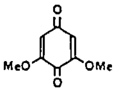
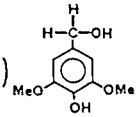
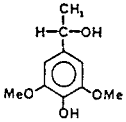
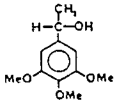
Mechanical treatment of syringylalcohol (1), α-methyl syringylalcohol (2), and 3,4,5-trimethoxyphenyl methylcarbinol (3).

In a recent study on the mechanochemical conversions of veratrylglycerol-β-syringaldehyde ether, Wu and Sumimoto[10] strongly suggested the generation of ultrasonic waves including $\cdot O_2H$, $\cdot OH$, and $\cdot H$ radicals in the aqueous media of mechanical treatment with CBM, VBM, or a laboratory refiner. The formation of $\cdot OH$ radicals in this media was recently confirmed and will be published shortly. In the present study, syringylalcohol (1), α-methyl syringylalcohol (2), 3,4,5-trimethoxyphenyl methylcarbinol (3), and syringylglycerol -β-guaiacyl ether (4) were synthesized and treated with CBM, VBM, and a laboratory refiner to find out the reaction mechanisms. Four compounds, (1)~(4), were dispersed onto filter paper pulp and treated with CBM or VBM (VBM-1) in aqueous media for 1h. In addition, compounds (1) and (2) were dispersed onto linter pulp, and treated with VBM (VBM-2) in aqueous media for 1h.

As shown in TABLE 1 and FIGURE 1, treatment of syringylalcohol (1) with CBM, VBM-1, and VBM-2 for 1 h yielded syringaldehyde (5), the corresponding *p*-carbonyl phenol, in yields of 1.3, 2.1, and 2.5 %, respectively. In addition, 3,5-dimethoxy-*p*-benzoquinone (7) was also produced by the treatment with VBM-1 and VBM-2 in yields of 0.4 and 0.5 %, respectively. Treatment of α-methyl syringylalcohol (2) for 1 h produced acetosyringone (6), in 0.6, 1.4, and 1.7 % yields, and 3,5-dimethoxy-*p*-benzoquinone (7) in tr., 0.2 and 0.3 % yields from CBM, VBM-1 and VBM-2 treatment, respectively. However, treatment of 3,4,5-trimethoxyphenyl methylcarbinol (3) with CBM, VBM-1, and VBM-2 for 1 h afforded acetosyringone (6) in 0, 0.2, and 0.3 % yields, respectively, but no *p*-benzoquinone (7) was found.

TABLE 1.

Yields of Conversion Products (5), (6), and (7) given by The Mechanical Treatment of Compounds (1),(2), and (3), respectively.

Starting Material	Condition	 (5)	 (6)	 (7) (%)
(1) 	CBM	1.3		—
	VBM-1	2.1		0.4
	VBM-2	2.5		0.5
(2) 	CBM		0.6	—
	VBM-1		1.4	0.2
	VBM-2		1.7	0.3
(3) 	CBM		—	—
	VBM-1		0.2	—
	VBM-2		0.3	—

Formation of acetosyringone (6) from compound (3) by the VBM-1 and VBM-2 treatments is apparently due to a replacement reaction of a *p*-methoxyl group by a • OH radical as shown in FIGURE 2. On the other hand, a • H radical abstraction from a phenolic OH group in compound [I] by • OH radical occurs first to give a phenoxy radical. Secondly, further abstraction of another • H radical at Cα by • OH radical can take place via an intermadiate [Ia] to give compound [II]. Thirdly, Dakin-type radical oxidation reaction of compound [II] is initiated by sequential addition of • H and • O_2H radicals to a *p*-carbonyl group [IIa] as was also mentioned in a previous paper[9]. Further oxidation proceeds via [IIb], [IIc], and [IId] to give both compound [III] and a carboxylic acid.

As shown in TABLE 1, the differences in the yields between VBM-1 and VBM-2 may be due to the difference between the relatively more rigid surface of VBM-2 and less rigid surface of VBM-1. Consequently, solid compounds dispersed onto linter pulp may be more effectively excited by the mechanical energy of collision to react

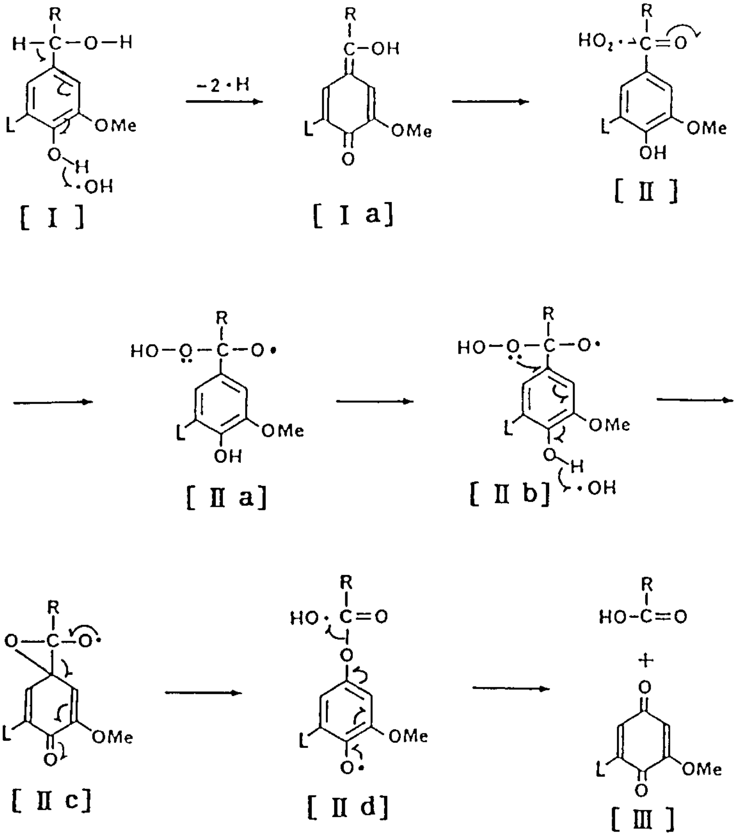


FIGURE 1. Conversion of *p*-carbinol [I] via *p*-carbonyl phenol [II] followed by Dakin-type radical oxidation to give *p*-benzoquinone [III].

with water-soluble ·O_2H, ·OH, and ·H radicals produced in the aqueous media of mechanical treatment.

Mechanical treatments of syringylglycerol-β-guaiacyl ether (4) with CBM, VBM-1, and a laboratory refiner.

As mentioned above, the treatment of syringyalcohol (1) and α-methyl syringylalcohol (2) as the simple 5-substituted type of model

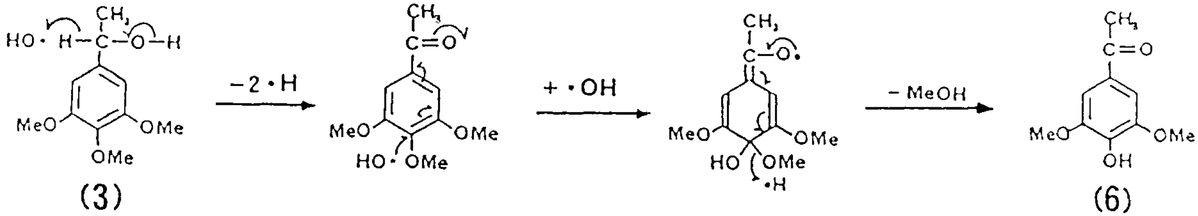


FIGURE 2. Replacement reaction of a *p*-OMe group by a • OH radical.

TABLE 2.

Yields of Mechanochemical Conversion Products from Model Compound (4).

*1: Yields of conversion products when 60 % of pulps were passed through 2nd refiner.

*2: Assumed yields of conversion products when 100 % of pulps were passed through 2nd refiner.

(weight %)

Condition	Recovery yields		(7)	(8)	(9)	(10)	(11)	(12)	sum
	Total	(4)							
CBM(air)	90.5	58.3	0.3	1.9	0.2	0.1	0	0	2.5
VBM(air)	81.8	50.5	1.4	4.3	0.8	1.3	0.1	0.6	8.5
VBM(N_2)	86.1	81.6	0.2	6.8	0.1	0.7	tr.	tr.	7.8
Refiner[*1]	54.3	44.9	1.0	3.0	0.6	0.9	0.1	0.4	6.0
〃 [*2]	90.5	74.8	1.7	5.0	1.0	1.5	0.2	0.7	10.3

*1: Yields of conversion products when 60 % of pulps were passed through 2nd refiner.

*2: Assumed yields of conversion products when 100 % of pulps were passed through 2nd refiner.

compounds with CBM or VBM furnished the corresponding *p*-carbonyl phenols (5) and (6), and 3,5-dimethoxy-*p*-benzoquinone (7) respectively. Therefore, syringylglycerol-β-guaiacyl ether (4) was synthesized and treated mechanically to study the reaction mechanism. Results given by the mechanical treatment of compound (4) are shown in TABLE 2 and FIGURE 3. First of all, treatment of compound (4) with CBM, VBM, and a laboratory refiner furnished α-(2-methoxyphenoxy)-β-hydroxypropiosyringone (8) as the major product. Although treatment of compound (4) with CBM afforded only four products, (7), (8), (9), and (10), treatment with either VBM or a laboratory refiner furnished two other products, (11) and (12). In the case of

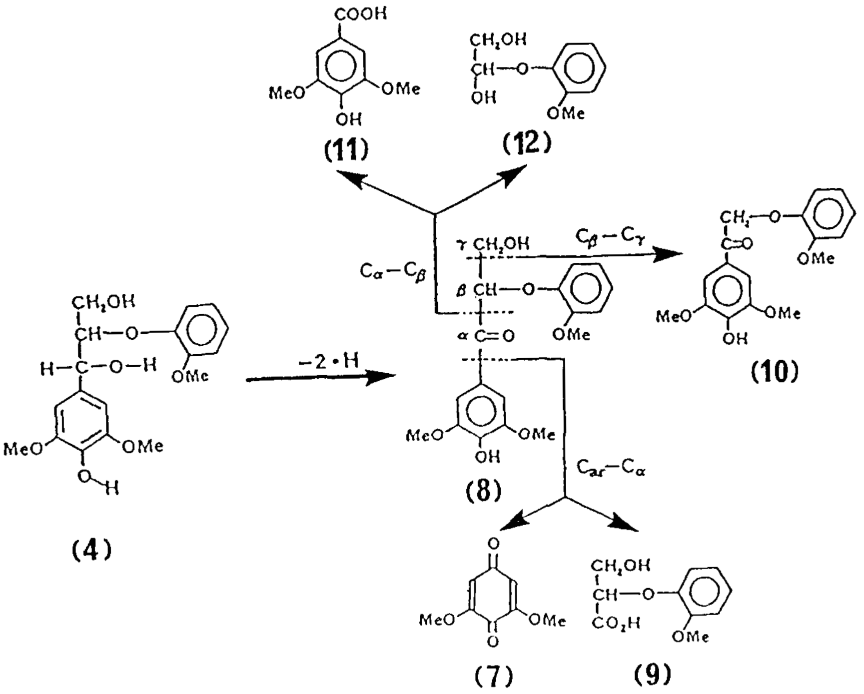


FIGURE 3. Mechanochemical conversions of compound (4).

the treatment of 50 g of "1R-pulps" homogeneously involving 1 g of compound (4) with KRK-refiner, about 60 % of "2R-pulps" were recovered, and therefore about 40 % of "2R-pulps" remained in the refiner. Consequently, the pulp recovery yields of 60 % was displayed by *1, and the assumed recovery yield of 100 % by *2, respectively. The assumed recovery yield incidentally approximated the yield from the treatment of compound (4) with VBM under air for 1h as shown in TABLE 2.

As mentioned in the previous section, simultaneous abstraction of • H radical from a phenolic OH group and another • H radical from $C\alpha$-H probably occurred to afford the corresponding *p*-carbonyl phenol (8). The latter could be followed by Dakin-type radical oxidation reaction to split Car-$C\alpha$, $C\alpha$-$C\beta$, and $C\beta$-$C\gamma$ bonds to give a pair of products of 3,5-dimethoxy-*p*-benzoquinone (7) and α-(2-methoxyphenoxy)-β-hydroxypropionic acid (9), and another pair of syringic acid (11) and (2-methoxyphenoxy)-1,2-dihydroxy ethane (12). Finally, α-(2-methoxyphenoxy)-acetosyringone (10) was provided by exclusion of HCHO.

As shown in TABLE 2, when the air in VBM containing compound (4) was replaced with nitrogen, the yield of compound (8) increased. While the yield of compounds (7), (9), (10), (11), and (12) decreased. These facts suggest that very few Dakin-type radical oxidation reactions can occur under a nitrogen atmosphere. However, the extremely high yields of compound (8) *i.e.* α-(2-methoxyphenoxy)-β-hydroxypropiosyringone in 6.8 % yield indicate the presence of a relatively high concentration of • OH radicals in the reaction media even under nitrogen. The highest total yields of 10.3 % was given by laboratory refiner *2. The second greatest yield of 8.5 % by VBM under air, and the third highest yield of 7.8 % by VBM under nitrogen.

Relationships between mechanochemistry of lignin and pulp bleaching.

In the present report, the mechanical treatment of compound (4), *i.e.* one of 5-substituted *p*-carbinol phenols [I] as a major component of lignin produces high amounts of *p*-carbonyl phenols [II] and lesser amounts of *p*-benzoquinones [III] as shown in FIGURE 1, 3, and TABLE 2. As mentioned in the Introduction, when *p*-carbonyl phenols [II] were treated with alkaline H_2O_2, considerable amounts of *p*-hydroquinones [IV] were obtained as a leuco-chromophore[3,4] (FIGURE 4).

The possible occurrence of *p*-benzoquinones [III] as a major chromophore was first suggested by Cole and Sarkanen[5] and later confirmed by Lee and Sumimoto[8] and others[9,10,12]. However, the chromophore [III] could be effectively degraded with alkaline H_2O_2 to give high brightness of the bleached pulps. High amounts of *p*-hydroquinones [IV] formed by the conventional bleaching cause intense color reversion, however, under irradiation with light to give *p*-

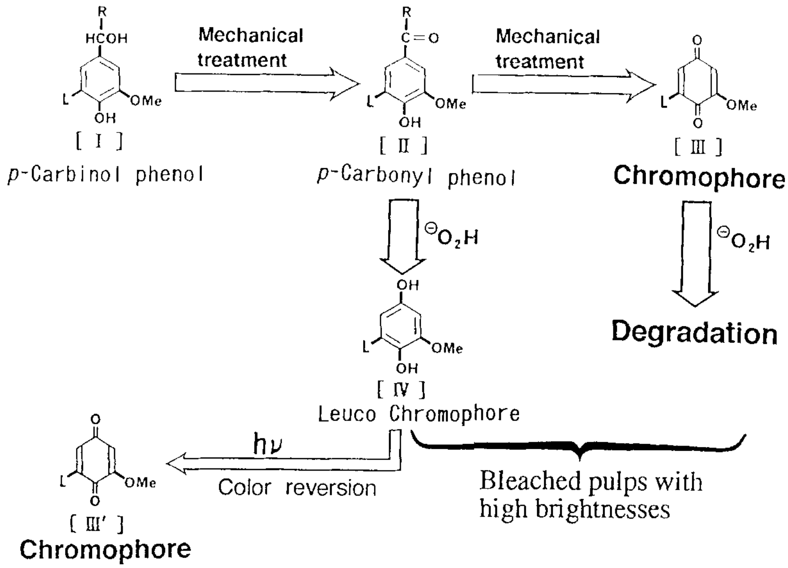


FIGURE 4. Significant relationships between mechanochemical conversions of lignin and the bleaching with alkaline H_2O_2.

benzoquinones [III'] [12]. Trials for another method of bleaching are therefore needed for the improvement of color reversion.

CONCLUSION

Treatment of syringylalcohol (1) and α-methyl syringylalcohol (2) with CBM under air for 1 h afforded 1.3 and 0.6 % of the corresponding p-carbonyl phenols (5) and (6), respectively. When treated with VBM-1 and VBM-2 under air for 1 h, both compounds (1) and (2) furnished 2.1 and 1.4 %, and 2.5 and 1.7 % of the corresponding p-carbonyl phenols (5) and (6), respectively. Treatment of compound (4) with CBM, VBM, VBM under nitrogen, and also with a laboratory refiner furnished 1.9, 4.3, 6.8, and 5.0 % of the corresponding p-carbonyl phenol (8) in the highest yields, respectively. These are probably followed by a complex Dakin-type radical oxidation with attack by $\cdot O_2H$ and $\cdot H$ radicals to the α-carbonyl groups yielding compounds (7) and (9) on the one hand and compounds (11) and (12) on the other hand. Significant relations of mechanochemistry of lignin to the present method of bleaching is also discussed.

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