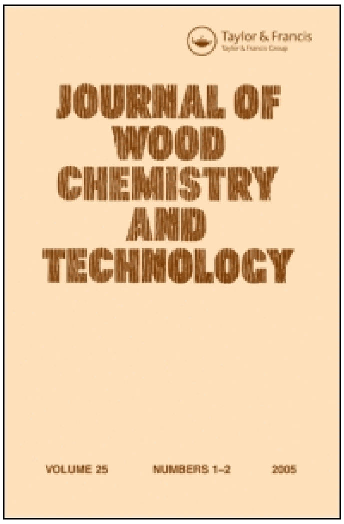

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Comparative Studies on the Mechanochemistry of Guaiacylglycerol- and Veratrylglycerol- β -Guaiacyl Ether

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COMPARATIVE STUDIES ON THE MECHANOCHEMISTRY OF GUAIACYLGLYCEROL- AND VERATRYLGLYCEROL- β - GUAIACYL ETHER. *

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ABSTRACT

Treatments of guaiacylglycerol- and veratrylglycerol-β-guaiacyl ether [I] and [II] with CBM, VBM and laboratory refiner furnished α-(2-methoxyphenoxy)-β-hydroxypropioguaiacone 1 as the major product in addition to a few small compounds 2-7 in relatively low yields. In addition, 5,5'-condensation reaction of compound [I] gave compounds 8, 9, and 10. Alternatively, Cα-Cβ splitting reaction of veratrylglycerol-β-guaiacyl ether [II] occurrs by the mechanical treatment to give a number of products (6,11-14, and 15). Compounds [II] also formed *p*-carbonyl phenol 1 and products 2, 4, and 7 by an alternate route. For comparison, mechanical treatments of vanillyl alcohol [III] ,α-methyl vanillyl alcohol [IV] , and veratryl alcohol [V] were made with a ceramic ball mill (CBM), vibration ball mill (VBM), respectively. Former two gave vanillin 15 and acetovanillone 16, but no product was found from veratryl alcohol [V] .

INTRODUCTION

Lee and Sumimoto reported that treatment of veratrylglycerol-β-guaiacyl ether[1] [II] with a ceramic ball mill (CBM) in air for 1h

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furnished almost no reaction product. In this case, no water was added to the reaction media. However, the treatment of veratrylglycerol-β-vanillin ether[1] with a ceramic ball mill (CBM) resulted in the Cα-Cβbond splitting to give large amounts of vanillin (a *p*-carbonyl phenol) and related products. When a phenylcoumaran derivative[2] having a *p*-carbonyl phenol group in the B-ring was treated in a CBM, a vibration ball mill (VBM) or a laboratory refiner, considerable amounts of stilbenes having a *p*-carbonyl phenol structure on its B-ring were obtained. Based on the results mentioned above, Lee and Sumimoto[3] suggested that a major cause of the intensive color reversion of bleached mechanical pulps may be due to the formation of 5-substituted *p*-hydroquinones. Wu and Sumimoto[4] recently reported on their results of treating veratrylglycerol-β-syringaldehyde ether with a VBM under air or nitrogen in the presence of water. Replacement of the air in a VBM by nitrogen resulted in slightly increased yields of syringaldehyde, a *p*-carbonyl phenol, but the yields of *p*-benzoquinone decreased dramatically. Considering all these proposed reaction mechanisms, the co-existence of • H, • OH, and • O_2H, generated by ultrasonic waves in the aqueous reaction media, was suggested.

As is well-known, the rolling shear which works inside the first refiner produces countless raw fibers in a second. Further rolling shear also works at the second refiner in a second again to give fine fibers having highly porous surfaces[5]. Defiberization processes in both first and second refining may, therefore, cause the violent emission of ultrasonic waves in the aqueous media, where vigorous sonolyses of lignin occur.

When syringylglycerol-β-guaiacyl ether was treated in a VBM for 1h[6], the yields of various conversion products almost corresponded to those with a laboratory refiner only in a second.

Mechanical treatments of both syringylglycerol-β-guaiacyl ether[6] and (5-5')-(β-*O*-4) type of lignin model compound[7] in the presence of water were recently made with CBM, VBM, and a laboratory refiner, respectively. Among the products, the corresponding *p*-carbonyl phenols were obtained in the highest yields, along with the corresponding *p*-benzoquinone and *p*-hydroquinone derivatives, respectively. The present study describes the mechanochemical conversions of two types of β-*O*-4 model compounds, namely guaiacylglycerol-β-guaiacyl ether [I] and veratrylglycerol-β-guaiacyl ether [II]. In addition, vanillyl alcohol [III], α-methyl vanillyl alcohol [IV], and veratrylalcohol [V] were mechanically treated for comparison.

EXPERIMENT

Separation and quantitative analyses of various mechanochemical conversion products (1 to 16) from model compounds [I -V] were accomplished by preparative thin layer chromatography (TLC) and high-pressure liquid chromatography (HPLC). Preparative TLC was performed on a glass sheet with a sillica-gel (kiselgel 60 PF$_{254}$) layer of 1.5 mm thickness. HPLC was performed on JASCO Triorotar-Ⅱ Chromatograph using a Chemcopack column (20 × 270 mm).

Identification of the reaction products was made through comparison of melting points (mp) and mixed mps with those of authentic samples, by the ultraviolet (UV) spectra, and direct inlet mass spectra (DI-MS) as well as proton nuclear magnetic resonance (^{1}H-NMR) spectra. 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 model compounds [I] , [Ⅱ] , [Ⅲ] , [Ⅳ] , and [V] .

Guaiacylglycerol-β-guaiacyl ether [I] and veratrylglycerol-β-guaiacyl ether [Ⅱ] were synthesized by the method of Itoh et al[6]. Vanillylalcohol [Ⅲ] and α-methyl vanillyl alcohol [Ⅳ] were made by reduction of vanillin 15 and acetoguaiacone 16, with sodium borohydride, respectively, under the combined use of phase transfer catalysts[8]. Veratrylalcohol [V] was commercially available.

Guaiacylglycerol-β-guaiacyl ether [I] ; DI-MS (70 eV) *m/z* (intensity, %) : 446 (1.1 M$^+$), 403(1.3), 360(2.1), 317(1.5); ^{1}H-NMR (400 MHz, $CDCl_3$) (acetate), δ(ppm) : 2.31 (9H, s, -OAc), 3.76(3H, s, aromatic-OMe), 3.81(3H, s, aromatic-OMe), 4.08(2H, m, γ -H), 4.15(1H, m, β -H), 4.83(1H, m, α-H), 6.86(4H, m, aromatic proton), 6.97(3H, d, J =1.5 Hz, aromatic proton).

Veratrylglycerol-β-guaiacyl ether [Ⅱ] ; DI-MS(70 eV) *m/z* (%): 334 (1.3 M$^+$), 303 (1.5), 211(3.6), 180(1.1); ^{1}H-NMR (400 MHz, $CDCl_3$) δ(ppm) : 3.83(3H, s, aromatic-OMe), 3.89(3H, s, aromatic-OMe), 4.02(3H, s, aromatic-OMe), 4.08(1H, m, β-H), 4.25(2H, m, γ -H), 4.97(1H, m, α-H), 6.91(4H, m, aromatic proton), 7.03(3H, d, J =1.5 Hz, aromatic proton).

Vanillyl alcohol [Ⅲ] ; DI-MS (70 eV) *m/z* (%): 184(100 M$^+$), 154 (12.7), 123(5.0).

α-Methyl vanillyl alcohol [Ⅳ] ; DI-MS(70 eV) *m/z* (%): 198(62.1, M^+), 183(58.5), 155(33.9), 123(67.6), 95(37.3), 43(100).

Treatment of Vanillylalcohol [Ⅲ] , α-methyl vanillyl alcohol [Ⅳ] and veratrylalcohol [Ⅴ] with CBM and VBM, respectively.

One hundred mg each of vanillylalcohol [Ⅲ] and α-methyl vanillylalcohol [Ⅳ] dissolved in 2 ml of acetone, respectively, 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 a VBM (SM-60, Yokohama Ind. Ltd. Co. 1 liter) and treated under air for 1h, respectively.

As a comparative experiment, 100 mg of veratrylalcohol [Ⅴ] was dispersed onto 0.2 g of filter paper pulp to which 2 ml of water was added and then treated in a VBM under air for 1h. Extraction of the reaction mixture in CBM or VBM was first done 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 vanillylalcohol [Ⅲ] were 90.6 mg (CBM) and 93.3 mg (VBM). The residues from α-methyl vanillylalcohol [Ⅳ] were 89.1 mg (CBM) and 91.5 mg (VBM), and from veratrylalcohol [Ⅴ] were 90.4 mg (CBM) and 93.6 mg (VBM). The resulting mixtures mentioned above were separated by HPLC (methanol:dichloromethane=1:9).

In this first experiment, 86.0 mg and 80.0 mg of vanillylalcohol [Ⅲ] were recovered from the residues in CBM and VBM, respectively. In addition, 0.5 mg and 1.0 mg of clear white crystals were obtained, respectively. These crystals had a mp of 80-82℃; DI-MS(70 eV) *m/z* (%): 152(15.9, M^+), 151(18.4), 91(100). Comparison of mp and mixed mp as well as DI-MS confirmed its identity as vanillin 15.

Treatment of 100 mg of α-methyl vanillylalcohol [Ⅳ] with CBM and VBM recovered 87 mg and 85 mg of the starting materials, respectively, and furnished 0.3 mg and 0.8 mg of colorless oil. DI-MS(70 eV) *m/z* (%): 196(25.3, M^+), 181(100), 165(28.1), 106(18.3). DI-MS spectrum showed that the oil was acetoguaiacone 16.

Treatment of 100 mg of veratrylalcohol [Ⅴ] with CBM and VBM the presence of water gave 90 mg and 88 mg of the starting materials, but no reaction product was identified.

Mechanical treatment of Compound [I] or [II] with either CBM or VBM.

One hundred mg of [I] or [II] dissolved in 2 ml of dichloromethane was dispersed onto 0.2 g of filter paper pulp, and the solvent was removed *in vacuo*. Two ml of water was then added and pulp treated with either CBM or VBM under air for 1h. Extraction of the reaction mixture in CBM or VBM was first done twice with 100 ml of methanol followed by two extractions with 100 ml of ethyl acetate. The residues obtained by the treatment of [I] with either CBM or VBM were 90.5 and 81.8 mg, respectively. The starting material [I] recovered was 58.3 mg (CBM) and 50.5 mg (VBM) by preparative TLC (benzene:ethyl acetate:formic acid =15:4:1). The residues were separated further by HPLC (methanol:dichloromethane=1:19), to find out the chemical structures 1 - 7 as shown in FIGURE 1a. These were accompanied by dimerization products 8 -10 as shown in Figure 1b, and the yields are shown in Table 1.

Treatment of [II] with either CBM or VBM gave 90.5 and 81.8 mg of the reaction mixture, respectively. The starting material [II] recovered was 59.6 mg (CBM) and 52.8 mg (VBM), with the residues further separated by HPLC to give the compounds shown in TABLE 2.

Treatment of Compounds [I] or [II] with a laboratory refiner.

As mentioned in the previous paper[8], we named the pulps which passed through only the first TMP refiner at an elevated temperature in a mill as "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 [I] or [II] dissolved in 5 ml of dichloromethane was dispersed onto 50 g of extractives-free "1R-pulps" , and the solvent then removed by stirring *in vacuo*. The resulting pulps were fed into an open type KRK-refiner for the second refining. Details of the treatment are described in the previous paper[8].

As shown in the following section, identification of the isolated compounds was made by standard methods. The yields of the identified compounds are shown in TABLE 1 and 2. For comparison, a second refining of the extractives-free "1R-pulps" was

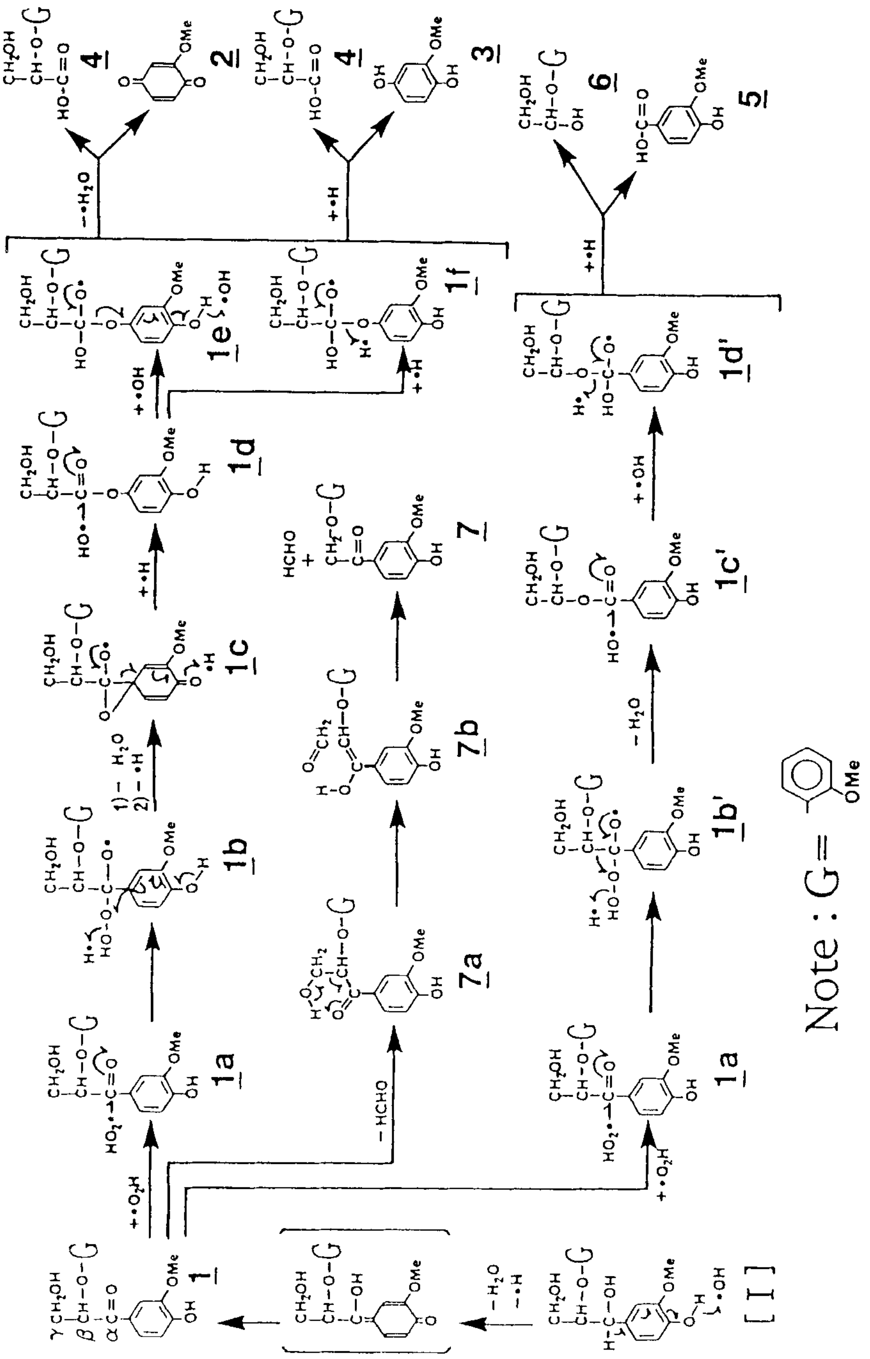

FIGURE 1a. Mechanochemical conversions of guaiacylglycerol-β-guaiacyl ether [I] .

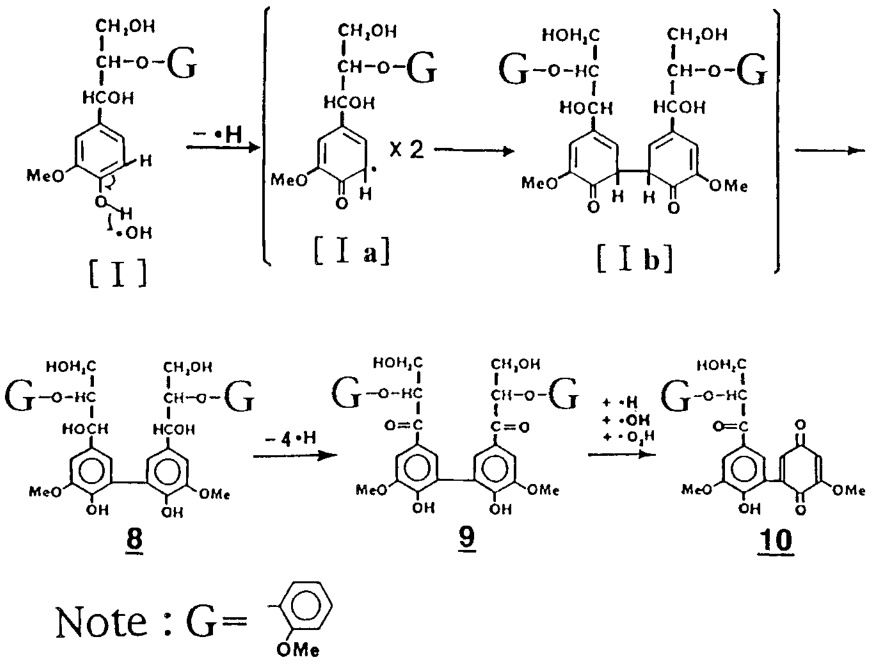

FIGURE 1b 5,5'-Condensation of guaiacyl glycerol-β-guaiacyl ether [I] and the following reactions.

TABLE 1.

Yields of mechanochemical conversion products from guaiacylglycerol-β-guaiacyl ether [I] .

(weight %)

Condition	Recovery yields		Mechanochemical conversion*1							5-5'-Condensation*2		
	Total	[I]	1	2	3	4	5	6	7	8	9	10
CBM(air)	89.3	50.1	1.3	tr.	tr.	0.2	tr.	tr.	0.2	tr.	0.1	0.1
VBM(air)	80.6	46.9	5.1	1.1	0.5	1.9	0.2	0.3	2.3	0.3	1.1	0.9
VBM(N_2)	83.1	58.8	6.7	0.2	0.1	0.3	tr.	tr.	1.0	0.5	1.3	1.0
Refiner*3	56.8	29.1	2.9	0.5	0.2	1.0	0.1	0.1	1.3	0.9	0.6	0.5
Refiner*4	94.9	48.6	4.8	0.8	0.3	1.7	0.1	0.2	2.2	1.5	1.0	0.8

*1 : See FIGURE 1a. *2 : See FIGURE 1b.

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

*4 : Assumed yields of conversion products when 100 % of 1R-pulps were passed through 2nd refiner.

TABLE 2.
Yields of mechanochemical conversion products from veratrylglycerol-β-guaiacyl ether [II] .

(weight %)

Condition	Recovery yields		Cα-Cβ Splitting *1						Oxidative process coupling*2				
	Total	[II]	6	11	12	13	14	15	1	2	4	7	CP*3
CBM(air)	91.1	85.2	0.3	0.2	0.3	0.1	0.8	0.2	0.2	0.1	0.1	0.1	0.3
VBM(air)	89.5	74.6	1.6	1.1	1.3	0.7	3.8	0.9	0.8	0.4	0.3	0.5	2.6
VBM(N_2)	90.4	75.9	0.5	0.7	0.8	0.4	4.0	1.4	1.0	tr.	tr.	0.2	4.0
Refiner*4	54.8	30.6	0.9	0.5	0.6	0.3	2.0	1.1	0.4	0.2	0.1	0.2	1.3
Refiner *5	91.6	78.3	1.5	0.8	1.0	0.5	3.3	1.8	0.6	0.3	0.1	0.4	2.1

*1 : See FIGURE 2a. *2 : See FIGURE 2b. *3 : Colored polymer.

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

*5 : Assumed yields of conversion products when 100 % of 1R-pulps were passed through 2nd refiner.

done using the same conditions as mentioned above. No identifiable compound was obtained.

Treatment of Compounds [I] or [II] under N$_2$ with VBM.

One hundred mg of lignin model compound [I] or [II] 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 then added to the resulting pulp placed in a VBM, the air in the VBM replaced three times by nitrogen in a glove box (Tokyo Air Engineering Inc.) and then treated by the usual manner for 1h. From the resulting reaction mixture, 81.6 mg or 82.5 mg of the starting materials, [I] or [II] , respectively, was isolated by preparative TLC and the residue separated by HPLC, respectively. Identification of the four conversion products was made by comparison of mp and mixed mp, DI-MS and ^{1}H-NMR spectra as discussed below. Yields of the identified products are shown in TABLE 1 and 2.

Identification of mechanochemical conversion products.

Fourteen conversion products 1-15 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 1 and 2.

α-(2-Methoxyphenoxy)-β-hydroxypropioguaiacone 1 : mp 93-94 ℃; DI-MS(70 eV) *m/z* (%): 402(6.9, M^+), 360(6.1), 300(20.5), 237(18.1), 151(100) ; ^{1}H-NMR (400 MHz, $CDCl_3$)(acetate),δ(ppm) : 2.31(6H, s, -OAc),3.76(3H, s, aromatic-OMe),3.81(3H,s,aromatic-OMe), 4.09(2H, m, CH_2), 4.31(1H, m, CH), 6.86-6.97(7H, m, aromatic proton).

2-Methoxy-*p*-benzoquinone 2 : DI-MS(70 eV) *m/z* (%): 138(19.3, M^+), 107(100), 50(30.5) ; UV $^{EtOH}_{max}$ (ε) 250 nm (2.0×10^4), 356 nm (2.3×10^3).

2-Methoxy-*p*-hydroquinone 3 : DI-MS(70 eV) *m/z* (%): 140(68.1, M^+), 138(50.6), 107(100), 50(30.5) ; UV $^{EtOH}_{max}$ (ε) 291 nm (4.0×10^3).

α-(2-Methoxyphenoxy)-β-hydroxypropionic acid 4: 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, $CDCl_3$) δ(ppm): 3.85(3H,s,-OMe),3.98(2H,d,*J* =1.8 Hz, CH_2), 4.61(1H, m, CH), 6.95(4H, m, aromatic protons).

Vanillic acid 5 : 90-92℃; DI-MS(70 eV) *m/z* (%): 168(100, M^+), 151(19.3), 124(11.8); ^{1}H-NMR(400 MHz, $CDCl_3$)δ(ppm): 3.81(3H,s,-OMe), 6.81(3H, d, *J*=1.5 Hz, aromatic protons).

(2-Methoxyphenoxy)-1,2-dihydroxy ethane 6 : 130-133℃;DI-MS(70 eV)(acetate) *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(6H ,s, -OAc), 3.56(3H ,s, -OMe), 4.05(2H,t,*J*=1.1 Hz, CH_2), 4.83(1H, m, CH), 6.99(4H, m, *J* =1.5 Hz, aromatic protons).

2-(2-Methoxyphenoxy)glycollic acid 7 : 70-72℃ ; DI-MS(70 eV) *m/z* (%): 288(20.5, M^+), 151(100), 137(10.5), 77(11.2); ^{1}H-NMR(400 MHz, $CDCl_3$)(acetate) ,δ(ppm): 2.39(3H,s,-OAc), 3.64(3H,s,aromatic-OMe), 3.81(3H,s,aromatic-OMe), 4.02(2H,s, CH_2), 6.83(3H, m, aromatic protons), 6.99(4H, m, aromatic protons).

Dehydro-bis-guaiacylglycerol-β-guaiacyl ether 8 : DI-MS(70 eV) m/z (%): 638(6.5, M$^+$), 576(4.8), 499(1.6), 422(2.1), 349(100), 227(10.5), 77(11.2); ^{1}H-NMR(400 MHz, CDCl$_3$)(acetate),δ(ppm):2.31-2.53(18H,m,-OAc), 3.72(6H,s,-OMe), 3.85(6H,s,-OMe), 4.09(2H, m, β-H), 4.16(4H, m, γ-H), 4.94(2H, m, α-H), 6.89(12H, m, aromatic protons).

Dehydro-bis- [α-(2-methoxyphenoxy)-β-hydroxypropioguaiacone] 9 : DI-MS(70eV) m/z(%): 574(7.3, M$^+$),512(3.8), 435(2.1),358(2.3), 285(100),163(12.6), 73(10.8); ^{1}H-NMR(400 MHz, CDCl$_3$)(acetate),δ(ppm): 2.33-2.59(12H,m,-OAc), 3.77(6H,s,-OMe), 3.81(6H,s,-OMe), 4.08(4H, m, CH), 6.71(12H, m, aromatic protons).

Quinoid compound 10 : DI-MS(70 eV) m/z (%): 426(19.3, M$^+$), 349(4.8), 212(1.6); UV λ_{max}^{EtOH} (ε) 259 nm (1.5 × 10^4), 318 nm (2.8 × 10^3).

Ethyleneglycol-guaiacyl ether 11 : 71-72℃ ; DI-MS(70 eV) m/z (%): 168(19.6, M$^+$), 137(100), 106(5.1), 77(10.3); ^{1}H-NMR(400 MHz, CDCl$_3$)(acetate),δ(ppm): 2.44(3H, m, -OAc), 3.85(3H, s, aromatic-OMe), 3.88(2H, d, J =1.8Hz, CH$_2$), 4.05(2H, d, J =1.3Hz, CH$_2$), 6.95(4H, m, aromatic protons).

Guaiacol 12: DI-MS(70eV)m/z(%)(acetate): 166(39.9, M$^+$), 123(10.8), 107(56.3), 81(100), 43(28.3); ^{1}H-NMR(400 MHz, CDCl$_3$)(acetate), δ (ppm): 2.21(3H,m,-OAc), 3.89(3H,s,aromatic-OMe), 7.26(4H, m, aromatic protons).

Glycol aldehyde 13 :DI-MS(70 eV)m/z (%)(acetate): 102(100, M$^+$), 59(55.1), 43(60.3); ^{1}H-NMR(400 MHz, CDCl$_3$)(acetate), δ (ppm): 2.16(3H,m,-OAc), 3.94(2H,d, J=1.8Hz, CH$_2$), 4.61(1H, m, CHO).

Veratryl alcohol 14:DI-MS(70 eV)m/z (%)(acetate): 167(100, M$^+$), 136(35.6), 105(58.6); ^{1}H-NMR(400 MHz, CDCl$_3$)(acetate), δ (ppm): 2.33(3H,m,-OAc), 4.06(2H,d, J=1.8Hz, CH$_2$), 3.64(3H,s,aromatic-OMe), 3.89(3H,s,aromatic-OMe), 6.99(3H, m, aromatic protons).

Vanillin 15 80-82℃ ; DI-MS(70 eV) m/z (%): 152(16.8, M$^+$), 151(19.5), 91(100); ^{1}H-NMR(400 MHz, CDCl$_3$)(acetate) ,δ(ppm): 2.39(3H,s,-OAc), 3.58(3H,s,aromatic-OMe), 4.61(1H, m, CHO), 6.99(3H, m, aromatic protons).

RESULTS AND DISCUSSION

Mechanical treatment of vanillylalcohol [III], α-methyl vanillylalcohol [IV], and veratrylalcohol [V].

In the present study, guaiacylglycerol-β-guaiacyl ether [I] and veratrylglycerol-β-guaiacylether [II] were synthesized and treated with CBM, VBM, and a laboratory refiner, respectively, to identify the reaction products and then propose possible reaction mechanisms. In addition, vanillylalcohol [III], α-methyl vanillyl alcohol [IV], and veratryl alcohol [V] were also treated to identify the products.

Treatment of vanillyl alcohol [III] with CBM or VBM for 1h furnished vanillin 15, the corresponding *p*-carbonyl phenol, in yields of 0.5 and 1.0 %, respectively. Another treatment of α-methyl vanillyl alcohol [IV] with CBM and VBM for 1h furnished acetoguaiacone 16 in 0.3 and 0.8 % yields, respectively. However, treatment of veratryl alcohol [V] with CBM and VBM for 1h recovered the starting material.

Formation of vanillin 15 and acetoguaiacone 16 by the treatments with CBM or VBM apparently occurred by abstraction of two • H from both the phenolic OH and Cα-H in compounds [III] and [IV] by two • OH.

Mechanical treatment of guaiacylglycerol-β-guaiacyl ether [I] with CBM, VBM, and a laboratory refiner.

As mentioned above, the treatments of both *p*-carbinol phenols [III] and [IV] with either CBM or VBM furnish the corresponding *p*-carbonyl phenols, vanillin 15 and acetoguaiacone 16, respectively. Therefore, guaiacylglycerol-β-guaiacyl ether [I] was synthesized and treated mechanically to determine the reaction mechanism. Results are shown in TABLE 1 and FIGURE 1a and 1b. Treatment of [I] with CBM, VBM, and a laboratory refiner in the presence of water afforded α-(2-methoxyphenoxy)-β-hydroxypropioguaiacone 1 in the highest yield (1.3 – 6.7 %) along with a number of other products. Although treatment of compound [I] with CBM afforded only five products (1, 4, 7, 9, and 10), treatment with either VBM or a laboratory refiner furnished five additional products (2, 3, 5, 6, and 8). When 50 g of "1R-pulps" homogeneously involving 1 g of compound [I] were treated with KRK-refiner, about 60 % of "2R-pulps" were recovered and about 40 % of "2R-pulps" remained in the refiner. Accordingly, the pulp recovery yields of 60 % was displayed by *1, and the assumed recovery yields of 100 % by *2, respectively, as shown in TABLE 1. The assumed recovery yield approximated the yield from the treatment of compound [I] with VBM under air for 1h, as shown in TABLE 1.

As mentioned in the previous section and shown in FIGURE 1a, simultaneous abstraction of two • H, one from a phenolic hydroxyl group and the second from Cα-H, occurs to form the corresponding *p*-carbonyl phenol 1. Dakin-type radical oxidation of this phenol 1 may be initiated by addition of • H and • O_2H to the *p*-carbonyl group to give 1b, which is followed by repetition of radical hydrolyses via 1c, 1d, 1e and 1f to give either 2-methoxy-*p*-benzoquinone 2 and α-(2-methoxyphenoxy)-β-hydroxypropionic acid 4 , or 2-methoxy-*p*-hydroquinone 3 and α-(2-methoxyphenoxy)-β-hydroxypropionic acid 4.

On the other hand, formation of the intermediate ester of 1b' via 1d' also proceeds to give vanillic acid 5 and (2-methoxyphenoxy)-1,2-dihydroxy ethane 6. In addition, 2-methoxyphenoxy-acetoguaiacone 7 was also obtained by the release of formaldehyde from compound 1.

As mentioned above, the proposed Dakin-type radical oxidation reaction of compound 1 first occurs by addition of both • H and • O_2H to the α-carbonyl group, which requires repetition of hydrolyses as shown in FIGURE 1a. In our series of papers, treatments of veratrylglycerol-β-syringaldehyde ether[4], α-(2-methoxyphenoxy)-β-hydroxypropiosyringone[9], syringylglycerol-β-guaiacyl ether[5], and (5-5')-(β-*O*-4) type of lignin model compound[7] with CBM, VBM, and a laboratory refiner, respectively, produced the corresponding *p*-carbonyl phenols. All of these reactions led to a Dakin-type radical oxidation reaction. Generally, Dakin-type radical oxidation reactions proceed with the aid of • O_2H, • OH, and • H. Without any one of these radicals, Dakin-type radical reaction would not occur. In other words, this type of radical reaction requires the generation of ultrasonic waves in the aqueous reaction media. As mentioned in the INTRODUCTION, Wu and Sumimoto[4] suggested mechanical treatment generates ultrasonic waves which from • O_2H, • OH, and • H in the aqueous media. Further confirmation of the occurrence of ultrasonic waves in the aqueous media will be published shortly.

Dimerization of guaiacylglycerol-β-guaiacyl ether [I] .

As shown in the previous paper[9], • H abstraction from a phenolic OH group in the molecule of creosol occurred by a • OH to give a dienone radical, two of which condensed to give 5,5'-dehydro-bis-creosol. Even at that time, however, a reasonable mechanism could be proposed. As shown in FIGURE 1b, abstraction of phenolic • H from compound [I] afforded a dienone radical [I a] , two of which may condense to give dehydro-bis-guaiacylglycerol-β-guaiacyl ether 8. The latter can then be oxidized further to give 5,5'-dehydro-bis-[α-(2-methoxyphenoxy)-β-hydroxypropioguaiacone] 9 with final oxidation leading to the quinoid compound 10.

Mechanical treatments of veratrylglycerol-β-guaiacyl ether [Ⅱ] with CBM, VBM-1, and a laboratory refiner.

Results given by the mechanical treatment of veratrylglycerol-β-guaiacyl ether [Ⅱ] with CBM, VBM, and a laboratory refiner in the presence of water are shown in TABLE 2 and FIGURE 2a and 2b.

According to Lee and Sumimoto[1], treatment of veratrylglycerol-β-guaiacyl ether [Ⅱ] with CBM in the absence of water gave almost no reaction product. However, treatment of veratrylglycerol-β-vanillin ether[1] with CBM afforded veratryl alcohol 14 in 5.5 % yield resulting in the cleavage of the Cα-Cβ bond. When veratrylglycerol-β-syringaldehyde ether[4] was treated with VBM in the presence of water, veratryl alcohol 14 in 7.4 % yield was obtained, presumedly by the Cα-Cβ splitting reaction. In the present report, the Cα-Cβ splitting reaction of [Ⅱ] first occurs to give veratryl alcohol 14 in 3.8 % yield as the major product. By another route, the mechanical treatment of [Ⅱ] affords *p*-carbonyl phenol 1 as the major product. A total of eleven products, including compounds 1, 2, 4, 6, 7, 11−15, and colored polymer (CP) were obtained.

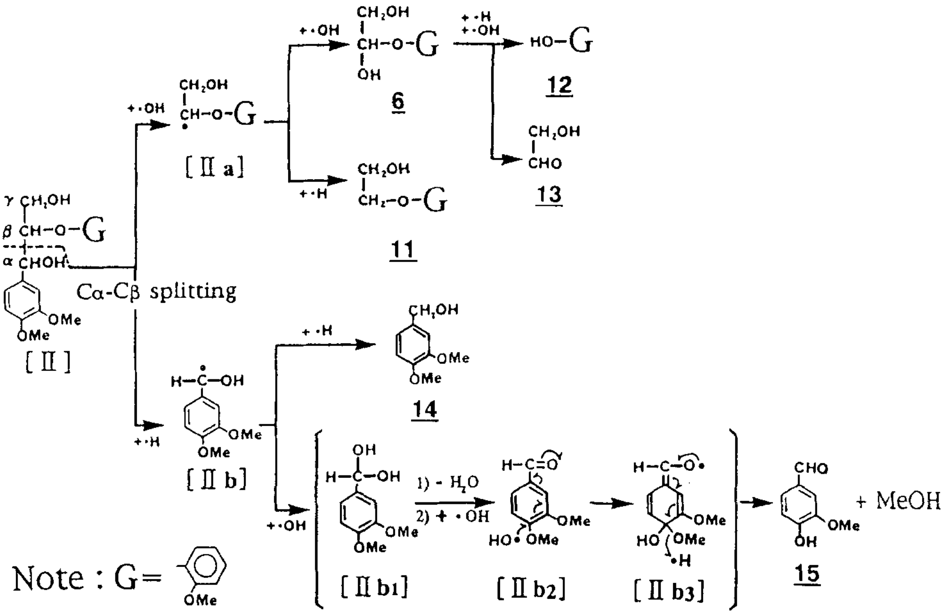

FIGURE 2a. Cα-Cβ splitting reaction of veratrylglycerol-β-guaiacyl ether [Ⅱ] and the following reaction.

As shown in FIGURE 2a, the Cα-Cβ splitting reaction of [Ⅱ] produces two radicals [Ⅱa] and [Ⅱb] . Addition of • H or • OH to the radical [Ⅱa] can lead to either (2-methoxyphenoxy)-1,2-dihydroxy ethane 6, or ethyleneglycol-guaiacylether 11 in the yields of 2.2 and 1.1 %, respectively, which can be hydrolyzed partially to give guaiacol 12 and glycolaldehyde 13, in the yields of 1.3 and 0.7 %, respectively. On the other hand, addition of • H or • OH affords veratryl alcohol 14 and vanillin 15, in the yields of 3.8 and 0.9 %, respectively.

As shown in FIGURE 2b, abstraction of a • H at Cα-H by • OH followed by homolytic substitution reaction of *para*-phenol ether group by • OH affords α-(2-methoxyphenoxy)-β-hydroxypropioguaiacone 1 via intermediates [Ⅱc] and [Ⅱd] . Addition of both • H and • OH to compound 1 furnishes 2-methoxy-*p*-benzoquinone 2 and α-(2-methoxyphenoxy)-β-hydroxypropionic acid 4. However, the difference in the yields between compound 2 and 4 suggested that

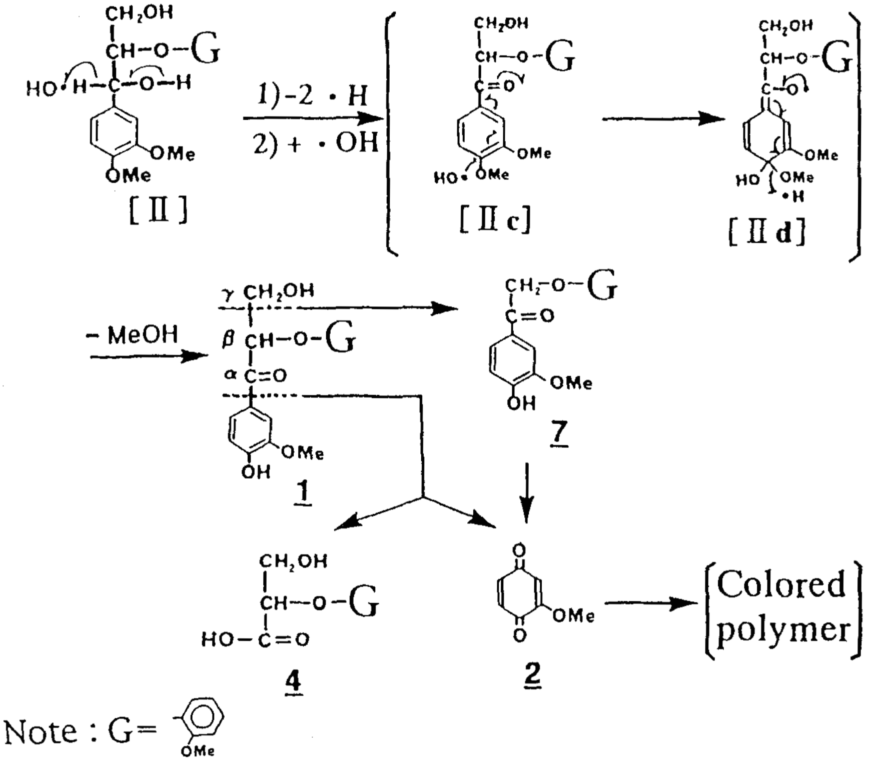

FIGURE 2b. Oxidative hydrolyses of veratrylglycerol-β-guaiacyl ether [II].

formation of compound 2 via α-(2-methoxyphenoxy)-acetoguaiacone 7 from compound 1 may also occur as shown in FIGURE 1a. In addition, condensation of 2-methoxy-*p*-benzoquinone 2 can result in the formation of complex products including a colored polymer. On the other hand, 7 was apparently formed by loss of HCHO from 1.

The formation of *p*-benzoquinone derivatives from wood lignin during pulping should result in a dark color to mechanical pulps. Furthermore, condensation of *p*-benzoquinone derivatives may result in the formation of complex colored polymers to lower the brightness of mechanical pulp.

CONCLUSION

1a) When guaiacylglycerol-β-guaiacyl ether [I] was treated with a VBM, abstraction of two • H, one from a phenolic hydroxyl group and another one from a Cα-H atom, apparently occurs to give the corresponding*p*-carbonyl phenol 1.

b) Dakin-type radical oxidation reaction of *p*-carbonyl phenol 1 takes place by first addition of both • H and • O_2H to the α-carbonyl group, which requires repeated hydrolyses via 1a and 1b, to give 2-methoxy-*p*-benzoquinone 2, 2-methoxy-*p*-hydroquinone3, and others.

c) Abstraction of a phenolic • H from [I] affords a dienone radical [I**a**], which is dimerized to give dehydro-bis-guaiacylglycerol-β-guaiacyl ether 8. The latter is further oxidized to 5, 5'- dehydro- bis- [α- (2- methoxyphenoxy) -β-hydroxypropioguaiacone] 9 and finally to the quinoid compound 10.

d) As shown in FIGURE 1a and 1b, Dakin-type radical oxidation proceeds only under the co-existence of • O_2H, • OH, and • H. Therefore, this suggests that ultrasonic waves are generated in the aqueous media.

2a) The Cα-Cβ splitting reaction of veratrylglycerol-β-guaiacyl ether [II] gives the intermediate radicals [II**a**] and [II**b**]. Compound [II**a**] then give (2-methoxyphenoxy)-1,2-dihydroxy ethane 6, ethyleneglycol-guaiacylether 11, guaiacol 12, and glycolaldehyde 13. Compound [II**b**] furnished veratryl alcohol 14 and vanillin 15.

b) Another route by which the mechanical treatment of Compound [II] affords *p*-carbonyl phenol 1 is through the simultaneous abstraction of two • H. The subsequent Dakin-type radical oxidation of *p*-carbonyl phenol 1 gives 2-methoxy-*p*-benzoquinone 2 and complex colored polymers.

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