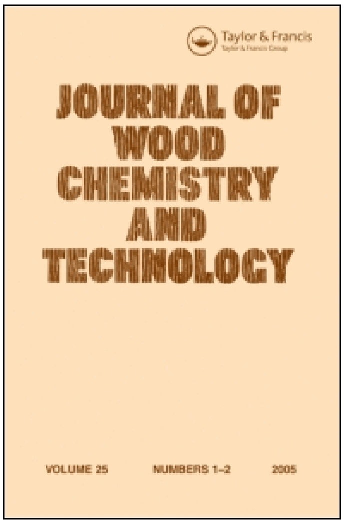
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A Characteristic Reaction of Lignin in Ionic Liquids; Glycelol Type Enol-Ether as the Primary Decomposition Product of *β*-*O*-4 Model Compound

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Abstract: Guaiacylglycerol-*β*-guaiacyl ether (GG), which contains a predominant inter-unit linkage of lignin, could be converted into a corresponding glycerol type enol-ether (EE), 3-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-2-propenol, by the heat treatment in ionic liquids. EE is believed to be the unstable intermediate of the lignin decomposition process under acidic and alkaline conditions. By contrast, EE could be isolated as a relatively stable compound from the reaction mixture of ionic liquids. EE was formed as a primary reaction product in all ionic liquids used in this research under the temperature conditions of 120°C, although the decomposition rate and secondary decomposition products of GG varied with the ionic liquid used. NMR data suggested that dehydration reaction of GG progressed stereospecifically and [Z] isomer was predominantly formed (stereoselectivety of [Z] is higher than 90%).

Keywords: Lignin model compound, ionic liquid, enol-ether, stereospecific dehydration, hydroboration-oxidation

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INTRODUCTION

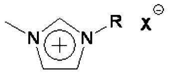
Lignocellulosic biomasses have been expected to be the most important biomass resources in the second generation biomass industries. Lignocelluloses are composed of carbohydrate polymers, cellulose and hemicelluloses, and lignin. Chemical and physical properties of carbohydrate polymers have been well identified. By contrast, polymeric structures of lignin are less understood in comparison with other components, due to its highly complex chemical natures. Milled wood lignin (MWL), has been widely used for lignin structural studies. MWL is mainly extracted from middle lamella, and may not represent total lignin structure because of its low yield.[1,2] MWL preparation process has been improved by the addition of an enzymatic decomposition step for carbohydrate polymers after ball milling. By this procedure, MWL yield was dramatically improved up to 95%.[3] However, some chemical structural changes were also suspected during the ball milling process in their report. Undesirable chemical structural changes of lignin during milling process might not be prevented,[4] although structural changes could be reduced by the addition of toluene during the milling process.[5] Quantitative ^{13}C-NMR studies for MWLs prepared by different milling techniques indicated that there were just slight differences in chemical structures between MWLs prepared using vibratory milling under N_2 and toluene, although MWL yield was higher in the former method (22.8%).[6] Vibratory milling for shorter period (2 days) was recommended for the MWL preparation rather than a rotary milling for longer periods (6 weeks). Chemical structures of MWL can be quantitatively characterized nondestructively by ^{13}C-NMR.[7] However, it will be difficult to monitor chemical structural changes of native lignin during milling process by ^{13}C-NMR, unless native lignin is isolated from wood without violent milling processes. Wet chemistry will be required to estimate changes in chemical structures of native lignin during the milling process. Modified DFRC method applied to Wiley and rotary milled woods revealed the chemical structural changes in lignin during the milling process.[5] Slight structural changes in lignin molecules were detected even after rotary milling for a short period (1 week), and the similar magnitude of structural changes were detected by the modified DFRC method until the milling period was extended to 4 weeks. Chemical structural changes of lignin could be minimized by the use of these gentle milling processes. However, MWL yield prepared under the mild conditions was not comparable to the traditional methods using vibratory mills. Recently, an effective process, EMAL, has been proposed for the lignin isolation using the combined method of mild milling and enzymatic treatment followed by mild acidolysis.[8,9] This method can achieve a high yield and a high purity preparation at the same time. In this method, however, rotary milling for 2 weeks was required to make the wood meal susceptible to enzyme. Moreover, acidolysis was first developed as a mild decomposition method for lignin structural analysis.[10,11] EMAL has potential to be the good method for lignin preparation. However, further research might be needed to achieve the structural stability of lignin molecules during the separation process.

Recent progress in green chemistry has made it possible to dissolve and/or decrystallize cellulose in ionic liquids under moderate conditions.[12–15] Therefore, ionic liquids might have potential to be utilized in the pretreatment of a lignin isolation process, instead of a milling process. Some researches have already been done to dissolve wood sample directly in ionic liquids. ^{13}C- and ^{1}H-NMR spectral data have been collected, and lignin dissolved in ionic liquids was reported to have similar chemical structures to MWL.[16,17] However, chemical structural changes of lignin during the dissolution process have not been examined, although the solubility of kraft lignin and some model compounds in ionic liquids were reported.[18] For this purpose, to utilize ionic liquids as the pretreatment tool for lignin preparation, structural stabilities of lignin model compounds have been examined. In this article, a characteristic reaction of guaicylglycerol-β-guaiacyl ether in ionic liquids will be introduced.

RESULTS AND DISCUSSION

Three ionic liquids used in this study are listed in Table 1 with their chemical structures. Both IL-I and IL-II are solids, and IL-III is a liquid at room temperature. However, at the processing temperature used in this research (120°C), all ionic liquids were in a liquid phase (Table 1) and GG was completely dissolved in them. HPLC chromatograms of heat-treated GG in three ionic liquids are shown in Figure 1. In all ionic liquids, GG gradually decomposed with extending processing time. Decomposition rate of GG was higher in IL-III compared with the other ionic liquids. After 20 h treatment, almost all GG in IL-III was decomposed to the ranges in UV detection error. By contrast, substantial amount of GG remained in IL-I and IL-II after 72 h treatment. The initial reaction product appeared on HPLC chromatograms for all ILs at the elution time of 10.1 min. Relative integration area of this peak was increased

Table 1. Ionic liquids used in this research

Ionic Liquid	R	X	Phase at Room Temp*	Ref.
				
IL-I: 1-Butyl-3-methylimidazolium Chloride	$-CH_2CH_2CH_2CH_3$	Cl	Solid (Tm=41°C)	1
IL-II: 1-Allyl-3-methylimidazolium Chloride	-C=C	Cl	Solid (Tm=55°C)	2
IL-III: 1-Ethyl-3-methylimidazolium Acetate	$-CH_2CH_3$	CH3C(=Q)Q	Liquid (Tm<-20°C)	3

*Enabling Technologies Ionic Liquids, ChemFiles **2005** Vol. 5(6)

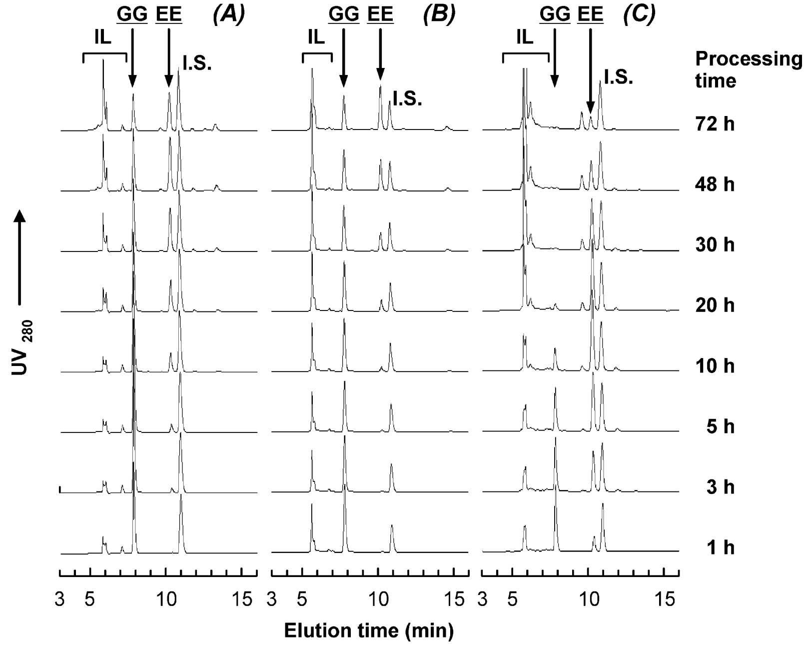


Figure 1. HPLC chromatograms of GG treated with ionic liquids. (A) with IL-I, (B) with IL-II, (C) with IL-III.

with decreasing GG. The peaks around 5–7 min were also increased with extending processing time. However, these peak increases were also observed in the blank (no GG added) reactions, and appeared as the large peak after 72 h treatment. Moreover, this peak could be removed as insoluble fractions on $CHCl_3$ extraction. Thus, this peak would be derived from ionic liquids. All ionic liquids were reported to be stable at this temperature. However, partial decomposition would gradually occur in the long processing time, although those decomposition products of ionic liquids have not been identified.

The initial reaction product was isolated by silica gel column chromatography after removing the ionic liquid by $CHCl_3$ extraction. Each fraction was checked by TLC, and fractions containing the initial reaction products were combined together. Good fractionation was confirmed by the HPLC analysis of this combined fraction, crude fraction (Figure 2).

From NMR spectra shown in Figure 3, the initial reaction product was identified as the α-β dehydration product of GG, 3-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-2-propenol, enol ether (EE) (detail assignment is shown in the next section). EE has been considered as an intermediate in lignin decomposition reactions under both alkaline[19,20] and acidic conditions[21] (Figure 4). However, this intermediate has not been identified due to its unstable

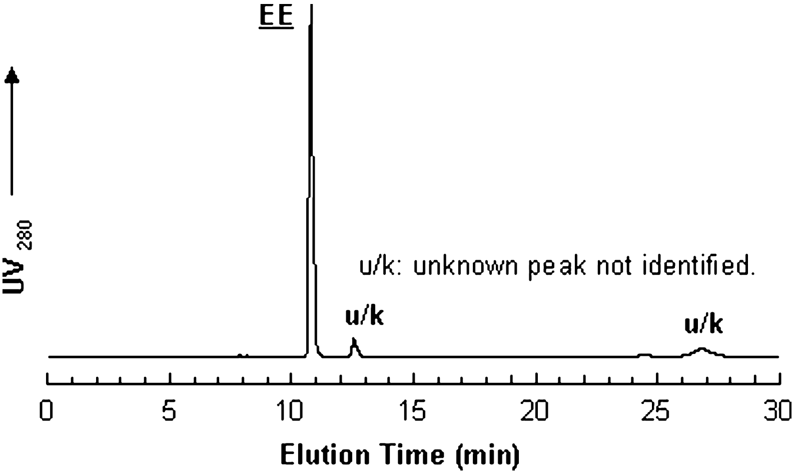


Figure 2. HPLC chromatograms of crude fraction of EE.

nature. Under the alkaline conditions, glycelol type enol ether is transformed into alkaline stable glycol type enol ether by the elimination of hydroxymethyl group as formaldehyde via quinonemethide intermediate. And, during the decomposition pathway of GG under acidic conditions, glycelol type enol ether is rapidly decomposed into guaiacol and Hibbert's ketone type compound. By contrast, EE was selectively formed as a primary decomposition product from GG in ionic liquids. Also, EE could be isolated as a relatively stable compound by simple solvent extraction with $CHCl_3$, although it was slowly decomposed in ionic liquids with extending processing time at the same temperature. Decomposition products of EE have not been identified in this study. However, HPLC analysis indicated that these secondary decomposition products of E-GG seemed to be varied depending on the ionic liquid used (Figure 1).

Glycerol type enol ether was chemically synthesized by the reduction of the acetate of the methyl ester of α-(2-methoxy-p-tolyloxy)-ferulic acid with $LiAlH_4$ by Lundquist and Lundgren.[21] Ralph et al. also reported that EE could be synthesized by the β-proton elimination of α-brominated ethyl *erythro*-3-hydroxy-3-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propanoate using DBU, followed by the reduction of γ-ethyl ester using DIBAL-H.[22] Due to the high stereoselective elimination of β-proton via quinonemethide indermediate, [Z] isomer was solely produced in the synthesis. Major signals on the ^{1}H- and ^{13}C-NMR spectra of EE prepared in this study were identical to the reported values by Ralph et al. These observation suggested that configuration of EE prepared by ionic liquid treatment of GG was a [Z] isomer. However, in our study, some minor signals also appeared

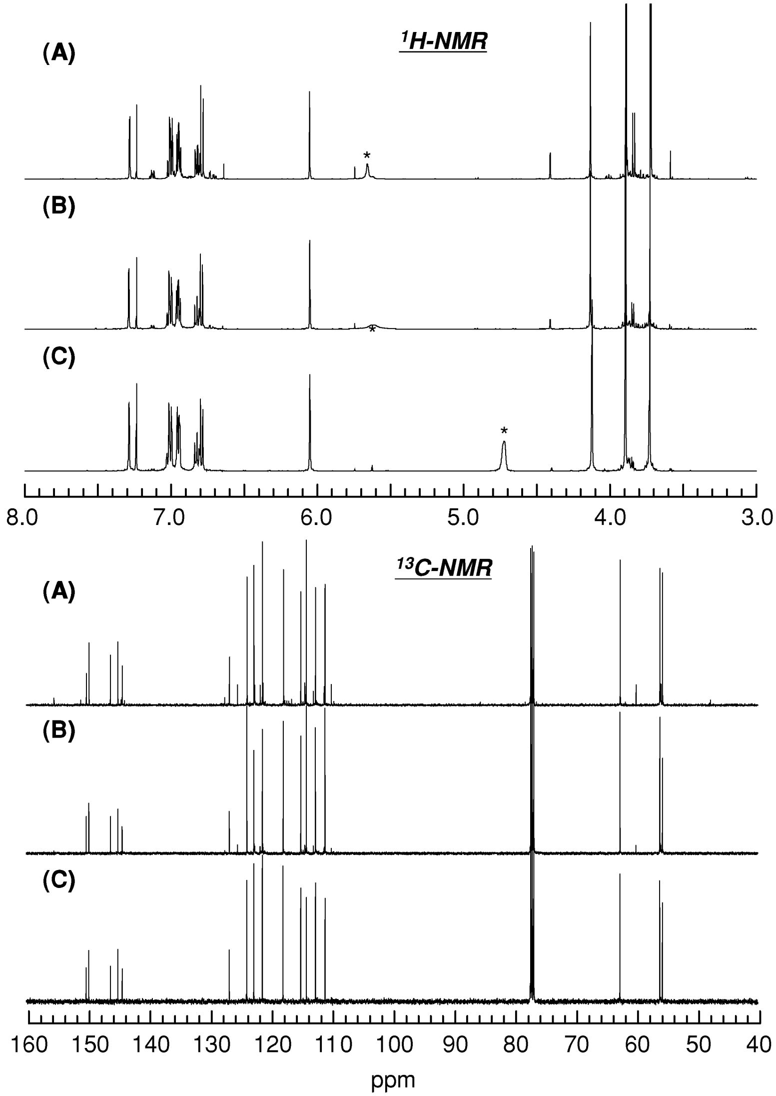


Figure 3. ^{1}H- and ^{13}C-NMR spectra of crude and purified initial decomposition products. (A): Crude Fraction, (B): Purified by re-crystallization, (C): Purified repeatedly using the chromatography.

at nearby regions of the main signals on NMR spectrum, although these minor signals could be reduced through the further purification process (Figure 4). Unfortunately, they could not be assigned because some of these minor signals were overlapped with major signals.

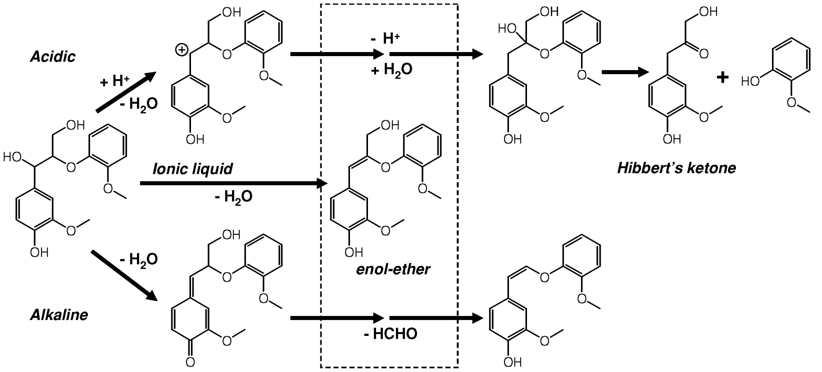


Figure 4. Decomposition pathway of phenolic β-O-4 lignin model compound through enol-ether intermediate under acidic and alkaline conditions, and in ionic liquids.

To identify this minor decomposition product in the crude fraction of EE, HMQC and HMBC spectrum were collected. Resolution of NMR analysis could be improved by these 2D techniques. In both HMQC and HMBC spectra, good correlations were confirmed for these minor signals in the same correlation patterns of major signals, although full assignment could not be achieved (Figure 5). Therefore, these minor signals might be assigned to an [E] isomer of EE, even though NMR data have not been available in literatures. Crude EE was isolated from the reaction mixture obtained in three different runs. The integration ratios of the signal appeared at 6.00 ppm, α-proton assigned for [Z]-EE, to the signal appeared at 5.75 ppm was slightly varied. However, maximum integration ratio of signal at 5.75 ppm to that at 6.00 ppm was less than 10%. Assuming that these minor signals on NMR spectrum could be assigned to [E]-isomer, relative isomer abundance was calculated as [E]/[Z] $>$ 0.1 from ^{1}H-NMR data.

It has not been easy to identify the minor decomposition product in the crude fraction directly. Therefore, formation of [E]-isomer in ionic liquid was examined by indirect method, hydroboration-oxidation of the crude fraction.[23] This anti-Markovnikov synaddition of hydroxyl group will lead to the selective formation of *erythro* and *threo* type GG from [Z] and [E] isomers, respectively (Figure 6). Both *erythro*-GG and *threo*-GG were well characterized in the literature.[24,25] Therefore, it would not be difficult to examine the stereo structure of EE from analytical data of GG derived by the hydroboration-oxidation reaction. Hydroboration-oxidation reaction was well adapted to EE, and signals appeared on the ^{13}C-NMR spectra of the reaction products could be clearly assigned to both *erythro*-GG and *threo*-GG, although some small unknown signals, which may relate with unlike sub-reaction products, also appeared (Figure 7). Signal intensity for *erythro*-GG was clearly higher than that for *threo*-GG. This observation would support that predominant stereostructure

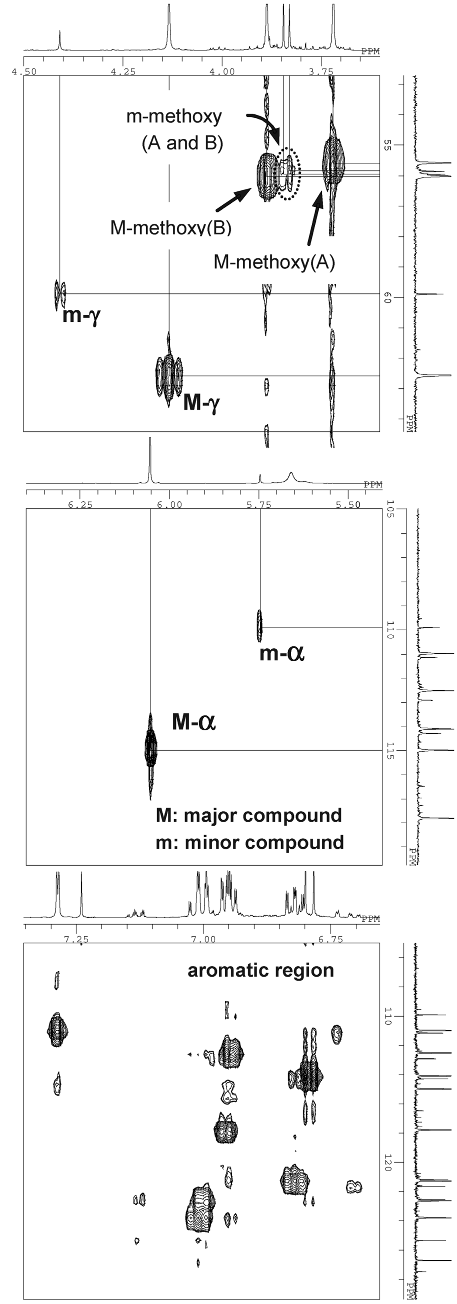


Figure 5. HMQC spectra of crude fractions of EE.

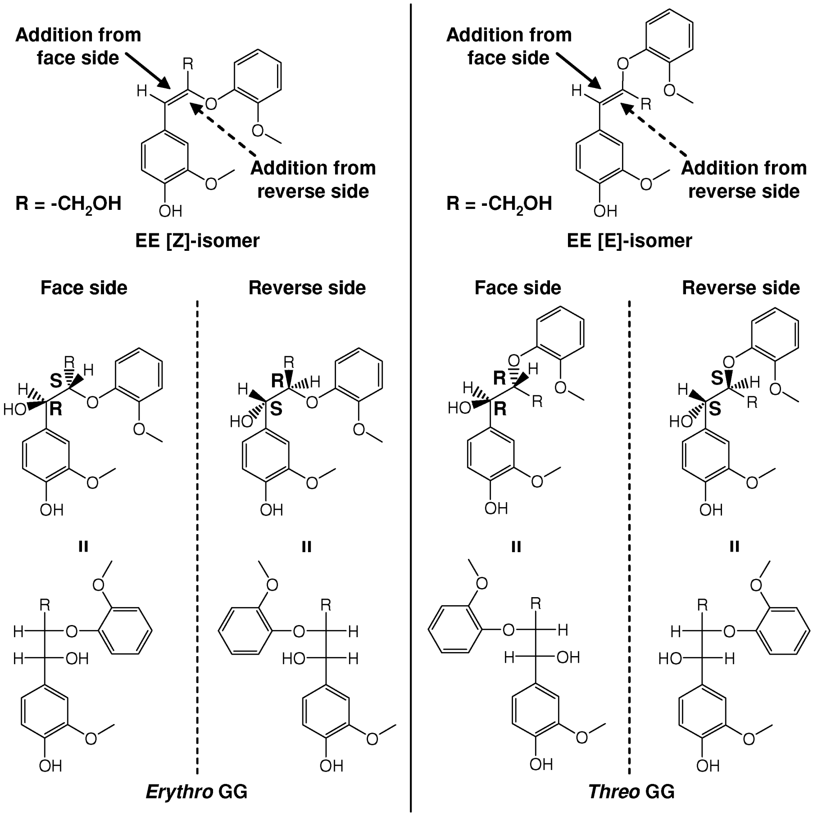


Figure 6. Hydroboration-oxidation reaction of EE.

of EE was [Z]-isomer. However, [E]/[Z] ratio estimated from hydroboration-oxidation products (*threo-/erythro*-GG ration) were not in accordance with the ^{1}H-NMR data for the crude fraction. Therefore, *threo-/erythro*-GG ration in the hydroboration-oxidation products was quantified by HPLC analysis. *Threo-* and *erythro*-GG could be separated by extending elution time using aqueous acetonitrile (acetonitrile/H_2O = 15/85). Calculated *threo-/erythro*-GG ratio by HPLC analysis was 24/76 in the crude fraction. However, even if the hydroboration was applied to purified [Z]-EE (purity $>$ 98%), *threo*-GG was also produced on the HPLC chromatogram (*threo-/erythro*-GG = 12/88). It has not been resolved why a larger proportion of *threo*-GG was produced by the hydroboration-oxidation. However, *threo/erythro* ratio was not changed even if the reaction period for H_2O_2 oxidation was extended. And, no isomerization of GG occurred under the H_2O_2 oxidation conditions used for hydroboration-oxidation. These observations indicated the isomer ratio was not changed after substrates were oxidized. Therefore, considering the reaction mechanism of

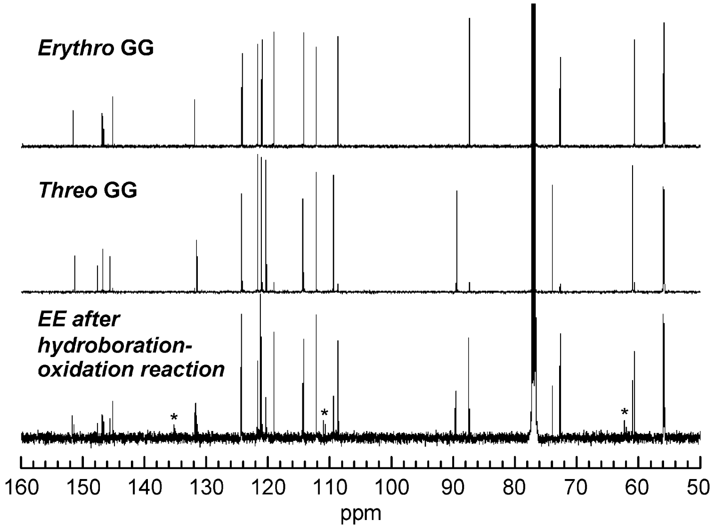


Figure 7. ^{13}C-NMR spectra of GG derived from EE by hydroboration-oxidation reaction.

hydroboration, production of *threo*-GG would indicate the formation of [E]-isomer of EE as the minor product in the ionic liquid. We believe that [E]-isomer could be separated from [Z]-isomer on HPLC analysis. However, we have not identified the certain peak for [E]-isomer on the HPLC chromatograms. Further experimention is required for equilibrium quantification of stereoisomers of EE, to confirm the formation of [E]-isomer of EE. Large-scale experiment will be required for GG using the same temperature conditions in the ionic liquids to isolate the minor decomposition products including secondary decomposition products to understand the structural stability and reactivity of lignin model compounds in ionic liquids.

CONCLUSIONS

EE, which has been considered to be an unstable intermediate in lignin degradation reactions in biomass conversion process, such as acidolysis and pulping, was produced as a stable compound in ionic liquids. In this α-β dehydration of GG, [Z] isomer was predominantly formed. A characteristic lignin might be produced by the biomass conversion using ionic liquids. Moreover, ionic liquids would be a good tool to synthesize enol-ether type lignin model compounds as well. In contrast, relatively high reactivity of lignin in ionic liquid would make it hard to isolate lignin having less-altered chemical structures from wood. In order to accomplish this goal, further studies are required to accumulate the better understanding about the reactivity of lignin in ionic liquids.

MATERIALS AND METHODS

Materials

IL-1 and IL-II were purchased from Wako-pure Chemicals (Japan), and IL-III was purchased from Sigma-aldrich Chem (USA). All ionic liquids were vacuum dried at 120°C before use. GG was purchased from Tokyo Chemical Industry Co. Ltd. (Japan), and used as received. This GG supplied from a chemical company having *erythro*-form was used for the reaction with ionic liquids. *Threo*-GG was synthesized in our laboratory in accordance with a previously published method.[26]

Reactions of GG in Ionic Liquids

Five mg of GG and 1 g of ionic liquid were put into the screw capped reaction tube and heated at 120°C using a dry heating block. After the certain period of heat treatment, reaction mixtures were replaced into the cold glass vials and 3,4,5-trimethoxybenzaldehyde solution was added as an internal standard for HPLC analysis. HPLC analysis was performed using HP 1100 Series (Agilent Technologies, CA) with Discovery C18 column (Supelco, PA). Mixed solvent of acetonitrile/H_2O was used as an eluent in various mixing ratio and UV at 280 nm was used as a detector.

Spectral Assignment of 3-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-2-propenol (EE)

To recover enough amount of EE for structural analysis, 100 mg of GG was mixed with 10 g of ionic liquids and treated under the same temperature conditions (120°C) in a reaction tube with mechanical stirring. After certain period of treatment, 48 h, 72 h, and 10 h for IL-I, IL-II and IL-III, respectively, 50 mL of water was added into the reaction mixture to reduce the viscosity of the solution for the effective extraction of the reaction mixtures with $CHCl_3$. $CHCl_3$ fractions were vacuum dried and fractionated by silica gel column chromatography using benzene/ethylacetate (10/3) as a mobile phase. Crude fractions containing EE were combined and EE was recovered by recrystallization from cold ether and washed with cold ether. NMR analyses were performed using JEOL α500 NMR. ^{1}H-NMR ($CDCl_3$-TMS at 25°C): δ 3.73 (3H, *s*, CH_3O-A3), 3.89 (3H, *s*, CH_3O-B2), 4.14 (2H, *s*, H-Cγ), 6.05 (1H, *s*, H-Cα), 6.80 (1H, *d*, J = 8.0 Hz, H-A5), 6.82 (1H, *m*, J = 8.0, 7.5, 1.5 Hz, H-B5), 6.95 (1H, *dd*, J = 5.0, 1.5 Hz, H-B3), 6.96 (1H, *dd*, J = 5.0, 1.5 Hz, H-B6), 7.01 (1H, *m*, H-A6), 7.02 (1H, *m*, H-B4), 7.29 (1H, *d*, J = 2.0 Hz, H-A2). ^{13}C-NMR ($CDCl_3$-TMS at 25°C) δ 55.61 (CH_3O-A3), 56.05 (CH_3O-B2), 62.61 (C-γ), 110.99 (C-A2), 112.54 (C-B3), 114.10 (C-A5), 114.99 (C-α), 117.87 (C-B6), 121.30 (C-B5), 122.66 (C-A6), 123.84 (C-B4), 126.72 (C-A1), 144.30 (C-B1), 144.99 (C-A4), 146.20 (C-A3), 149.76 (C-β), 150.22 (C-B2). MS m/z (relative intensity): 302 (M^+, 100), 244 (23), 211 (57), 124 (32).

Hydrobolation-Oxidation of EE

To a solution of EE (5 mg) in dry THF (100 ul), 200 μL of BH_3 solution (2M anhydrous THF) was added in a dry box. The reaction mixture was stored in a cold bath adjusted at 0°C for 150 min. After the reaction, 25 μL of 3M NaOH and 25 μL of 30% H_2O_2 were added and maintained over night at room temperature. The reaction mixture was acidified to pH ~3.0 with 0.1M HCl and extracted with $CHCl_3$. Organic layer was dried over Na_2SO_4 and $CHCl_3$ was removed by evaporation to dryness. NMR measurement was performed in $CDCl_3$ for the crude reaction mixture without purification.

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