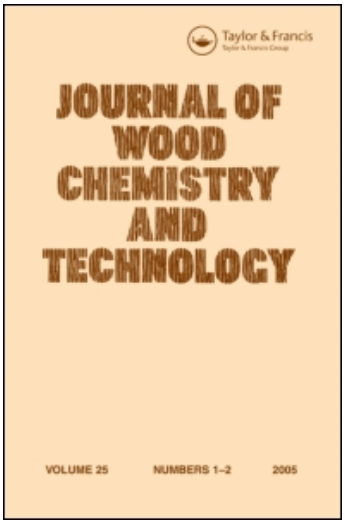

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Haruo Kawamoto[a]; Shiro Saka[a]
[a] Graduate School of Energy Science, Kyoto University, Kyoto, Japan

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Role of Side-Chain Hydroxyl Groups in Pyrolytic Reaction of Phenolic β-Ether Type of Lignin Dimer

Haruo Kawamoto and Shiro Saka
Graduate School of Energy Science, Kyoto University, Kyoto, Japan

Abstract: Role of side-chain hydroxyl groups in pyrolytic reaction of phenolic β-ether type of lignin dimer was studied with several regiospecifically methylated dimers under the pyrolysis conditions (N_2/400°C/1 min). Methylation of both C_α- and C_γ-hydroxyl groups reduced the C_β-O cleavage reactivity up to the level of the non-phenolic type. To maintain the high reactivity of guaicylglycerol-β-guaiacyl ether, at least one hydroxyl group was required in the side-chain. These results indicate that one hydroxyl group at C_α- or C_γ-position acts as a hydrogen donor during pyrolysis. Influence on the product formation also indicated that the hydrogen bond types affect the reaction sequences between the C_γ-elimination followed by the C_β-O cleavage and the C_β-O cleavage via quinone methide intermediate.

Keywords: Lignin, model dimer, regiospecifically methylated, pyrolysis, β-ether, cleavage mechanism, side-chain, hydroxyl group, hydrogen bond

INTRODUCTION

Molecular mechanism of the pyrolysis reaction of woody biomass is important as a fundamental principle of the thermochemical conversion processes such as carbonization, fast pyrolysis and gasification. In lignin pyrolysis,

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Address correspondence to Haruo Kawamoto, Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan. E-mail: kawamoto@energy.kyoto-u.ac.jp

understanding the pyrolysis behaviors of substructures including ether and condensed types of linkages is necessary to understand the overall pyrolysis of lignin macromolecule. Beta-ether linkage is the most important structure in lignin pyrolysis because this is the most abundant structure in lignin. This linkage has been reported to be cleaved in heat treatment, which results in the depolymerization of lignin.[1–3] Furthermore, model compound studies have indicated that the phenolic β-ether dimer is much more reactive than the nonphenolic one.[2,3]

Kawamoto et al.[3] have reported that pyrolytic decomposition of guaiacylglycerol-β-guaiacyl ether and veratrylglycerol-β-guaiacyl ether includes the two types of the reactions, that is, the C_β-O cleavage to form cinnamyl alcohol and the C_γ-elimination to give vinyl ether (Fig. 1). High reactivity of the phenolic dimer has been explained with the quinone methide formation, which makes the homolytic C_β-O cleavage and C_γ-elimination much easier, from the experimental results of α-ether and α,β-diether types of model compounds with various *p*-substituents in the C_α-phenoxy groups.[4] Contrary to this, Kawamoto et al.[5] also reported that deoxygenation of one hydroxyl group of the side-chain C_α or C_γ in the phenolic β-ether dimer substantially reduced the reactivity up to the level of the nonphenolic dimer. These results are conflicting since the phenolic C_α-OH (C_γ-deoxy) type is also expected to form quinone methide intermediate. In our previous study with various deoxygenated dimers,[5] the role of C_γ-OH has been explained by introducing the hypothesis that the hydrogen bonds between C_α- and C_γ- hydroxyl groups enhance the quinone methide formation (an ionic reaction) through stabilizing the transition state.

In this paper, role of side-chain hydroxyl groups in phenolic β-ether dimer during pyrolysis is presented, which was studied with various regiospecifically methylated dimers.

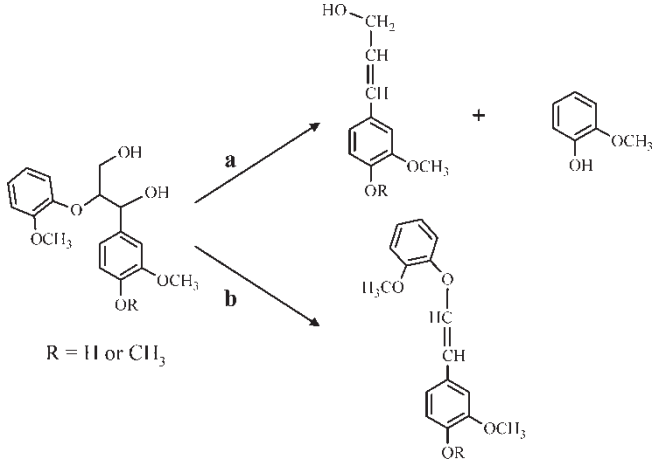


Figure 1. Pyrolytic pathways of β-ether type of model dimer.

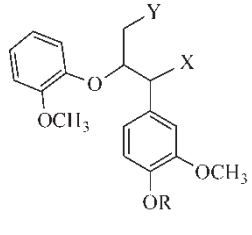
EXPERIMENTAL

Preparative thin layer chromatography (TLC) was conducted on silica gel plate (Kieselgel 60 F_{254}, Merk). High performance liquid chromatography (HPLC) was carried out with Shimadzu LC-10A under the following chromatographic conditions (column: STR ODS-II, flow rate: 0.7 ml/min, eluent: $MeOH/H_2O = 30/70 \rightarrow 100/0$ $(0 \rightarrow 40$ min), $100/0(10$ min), detector: UV_{254nm}, temperature: 40°C). Proton magnetic resonance (^{1}H-NMR) spectra were recorded in $CDCl_3$ with Varian AC-300 (300 MHz) spectrometer with tetramethylsilane (TMS) as an internal standard. Chemical shift and coupling constant are shown in δ and Hz, respectively.

Materials

Lignin dimers **1–6** (Fig. 2) were used in this study. 1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (guaicylglycerol-β-guaiacyl ether **1**),[3] 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (veratrylglycerol-β-guaiacyl ether **6**)[3] and 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-propanol (γ-deoxy dimer **5**)[5] are described in the previous papers. Three regiospecifically methylated dimers, 3-(4-hydroxy-3-methoxyphenyl)-3-methoxy-2-(2-methoxyphenoxy)-1-propanol (α-OMe dimer **2**), 1-(4-hydroxy-3-methoxyphenyl)-3-methoxy-2-(2-methoxyphenoxy)-1-propanol (γ-OMe dimer **3**) and 1,3-dimethoxy-1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propane (α,γ-diOMe dimer **4**) were prepared according to the synthetic routes in Fig. 3, starting from the β-hydroxy ester **7** (*erythro* isomer) which is an intermediate for the preparation of dimer **1**.[6]

α-OMe dimer **2** was prepared by methylation of compound **7** and the following reduction with $LiAlH_4$ and hydrogenolysis on 10% Pd-C. γ-OMe dimer **3** was prepared by successive benzylation, $LiAlH_4$ reduction, methylation and hydrogenolysis. α,γ-diOMe dimer **4** was prepared by methylation of the $LiAlH_4$ reduction product of compound **7** and subsequent



	R	X	Y
1	H	OH	OH
2	H	OCH_3	OH
3	H	OH	OCH_3
4	H	OCH_3	OCH_3
5	H	OH	H
6	CH_3	OH	OH

Figure 2. Model dimers used in this study.

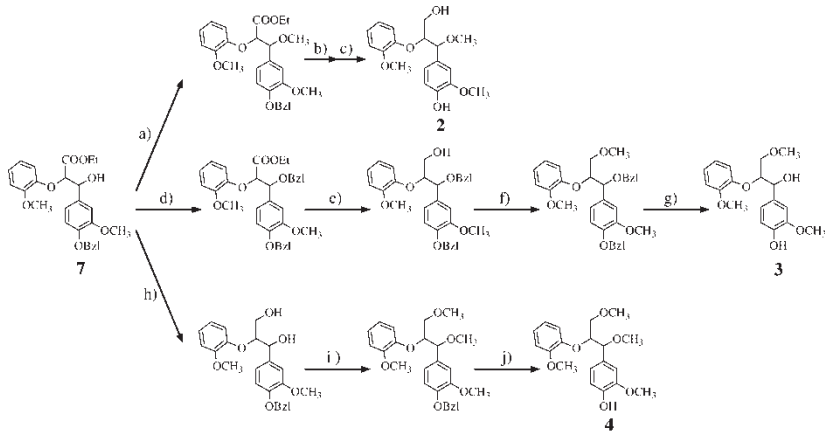


Figure 3. Synthetic routes for dimers **2**–**4**.

hydrogenolysis. Dimers **1**–**4** and **6** were obtained as *erythro* isomers. Structure of dimers **2**–**4** was identified with their ^{1}H-NMR spectra described in the following.

*Dimer **2** (erythro isomer)*: ^{1}H-NMR ($CDCl_3$): δ 3.28 (3H, s, OCH_3), 3.80, 3.85 (6H, 2s, OCH_3), 3.86 (2H, m, C_γ-H), 4.05 (1H, m, C_β-H), 4.39 (1H, d, $J = 7.0$, C_α-H), 5.59 (1H, broad s, phenolic OH), 6.5–7.0 (7H, m, arom.-H).

*Dimer **3** (erythro isomer)*: ^{1}H-NMR ($CDCl_3$): δ 3.33 (3H, s, OCH_3), 3.43 (1H, dd, $J = 3.8$, 10.5, C_γ-H), 3.63 (1H, dd, $J = 6.4$, 10.5, C_γ-H), 3.86, 3.89 (6H, 2s, OCH_3), 4.33 (1H, m, C_β-H), 4.85 (1H, d, $J = 4.1$, C_α-H), 5.59 (1H, broad s, phenolic OH), 6.7–7.1 (7H, m, arom.-H).

*Dimer **4** (erythro isomer)*: ^{1}H-NMR ($CDCl_3$): δ 3.28, 3.37 (6H, 2s, OCH_3), 3.60 (1H, dd, $J = 3.2$, 10.1, C_γ-H), 3.72 (1H, dd, $J = 5.2$, 10.1, C_γ-H), 3.75, 3.84 (6H, 2s, OCH_3), 4.4 (2H, m, C_α-H, C_β-H), 5.58 (1H, broad s, phenolic OH), 6.7–7.0 (7H, m, arom.-H).

Pyrolysis and Product Analysis

Pyrolysis was conducted with the experimental setup as previously reported,[3] which contains a round flask (volume: 20 ml) with a glass tube (120 mm long and 14 mm in diameter) for trapping the volatile products and a nitrogen bag attached through a three-way tap. With this system, volatile products are

effectively recovered at the cooling tube without suffering significant secondary pyrolysis reactions.

Dimer (10 mg) was placed at the bottom of the flask by evaporating the solution in MeOH (2.0 ml), and the air in the system was replaced with nitrogen. Pyrolysis was conducted by inserting the flask in a salt bath ($KNO_3/NaNO_3 = 1/1$, w/w) for 1 min, which was preheated at 400°C. After pyrolysis, the flask was immediately cooled with air flow for 30 s and subsequently in cold water, and then the reaction system was opened to release the gaseous products. The reaction mixture was extracted with THF (5.0 ml) twice to give THF-soluble fraction. This fraction was analyzed with HPLC with *p*-dibromobenzene as an internal standard. Coniferyl alcohol, coniferyl alcohol γ-methyl ether, guaiacol and 2-(2-methoxyphenoxy)-1-(4-hydroxy-3-methoxyphenyl)ethene were identified with the ^{1}H-NMR spectra of the isolated compounds compared with those of the authentic compounds. The product yield (mol%) is shown as the value based on the dimer used in this experiment.

RESULTS AND DISCUSSION

Table 1 summarizes the dimer recovery and the yields of some identified products after 1 min pyrolysis of dimers **1**–**6** in N_2 at 400°C. The results of dimers **1**, **5** and **6** are already reported in the previous papers.[3,5] Guaiacol is the product which indicates the β-ether cleavage. Reactivity indicated from the dimer recovery and the guaiacol yield varies depending on the dimer structure including the methylation site.

The dimer recovery (92.0%) and guaiacol yield (7.8%) for α,γ-diOMe dimer **4** are rather similar to those of nonphenolic dimer **6** and γ-deoxy

Table 1. Recovery of dimer and yields of some isolated products from dimers **1**–**6** (N_2/400°C/1 min)

					Products (mol%)		
	R	X	Y	Recovery of dimer (%)	Guaiacol	1-Phenylpropene	Vinyl ether
1[a]	H	OH	OH	49.7	50.1	30.4[b]	trace[f]
2	H	OCH_3	OH	82.0	17.5	1.7[b]	1.1[f]
3	H	OH	OCH_3	67.0	32.3	11.7[c]	nd[h]
4	H	OCH_3	OCH_3	92.0	7.8	1.7[c]	nd
5[a]	H	OH	H	92.1	3.5	1.7[d]	nd
6[a]	CH_3	OH	OH	91.6	3.1	0.5[e]	0.6[g]

[a]reference [5]; [b]coniferyl alcohol; [c]coniferyl alcohol γ-methyl ether; [d]isoeugenol; [e]4-*O*-methyl coniferyl alcohol; [f]2-(2-methoxyphenoxy)-1-(4-hydroxy-3-methoxphenyl)ethene; [g]2-(2methoxyphenoxy)-1-(3,4-dimethoxypheny1)ethene; [h]not detected.

dimer **5**. Thus, methylation of both hydroxyl groups in the side-chain reduces the reactivity of guaicylglycerol-β-guaiacyl ether (**1**) up to the level of the nonphenolic dimer **6**. Contrary to this, α-OMe dimer **2** and γ-OMe dimer **3**, both of which have one hydroxyl group in the side-chain, retain some enhanced reactivity compared to the nonphenolic type **6**, as indicated from the dimer recoveries [82.0% (**2**), 67.0% (**3**)] and the guaiacol yields [17.5% (**2**), 32.3% (**3**)]. These results indicate that at least one hydroxyl group in the side-chain is required to maintain the high β-ether cleavage reactivity of the phenolic dimer. These results are explainable by assuming that one hydroxyl group acts as a hydrogen donor during pyrolysis. Although further study is necessary on the possibility of the hydrogen bond at such high temperature (400°C) since hydrogen bond is not so effective at high temperature, hydroxyl – hydroxyl or hydroxyl – methoxyl type of hydrogen bond may be involved in the pyrolysis of these dimers. At ambient temperature, X-ray diffraction,[7,8] molecular simulation[9–13] and NMR studies[14,15] have indicated the intramolecular hydrogen bonds between C_α- or C_γ-OH and $-O_{methoxy}$ in the C_β-phenoxy group and between C_α- and C_γ-hydroxyl groups in the β-ether type of lignin dimer. These hydrogen bonds would stabilize the transition state of the quinone methide formation, which is the key intermediate for the low temperature homolysis of the C_β-O bond. Similar activation by the hydroxyl group has also been reported for the pyrolysis of β-hydroxy ketones and β-hydroxy olefins, and these results have been explained with the cyclic transition mechanism.[16–18] Under the pyrolysis conditions, where stabilization of the ionic products by solvation is not expected, such intramolecular stabilization of the transition state would be important to promote the ionic reaction including the quinone methide formation.

1-Phenylpropene and vinyl ether are expected to be formed through homolytic C_β-O cleavage (pathway **a**) and Cγ-elimination (pathway **b**), respectively, as shown in Fig. 1. These product formation also varied depending on the methylation site. γ-OMe dimer **3** gave 1-phenylpropene (coniferyl alcohol γ-methyl ether) in 11.7% yield along with guaiacol (32.3% yield). 1-Phenylpropene is reported to be unstable under these pyrolysis conditions to form polymerized products.[19] Thus, this 11.7% yield of 1-phenylpropene indicates that the pathway **a** is very important in the pyrolysis of γ-OMe dimer **3**. Contrary to this, the yield (1.7%) of 1-phenylpropene (coniferyl alcohol) from α-OMe dimer **2** is comparatively very low, and this is rather close to the yields of γ-deoxy dimer **5** (1.7%) and the nonphenolic dimer **6** (1.7%). These results indicate that the pathway **a** is inhibited in the pyrolysis of α-OMe dimer **2**. Nevertheless, a fair yield (17.5%) of guaiacol was obtained from dimer **2** as a C_β-O cleaved product. Thus, other C_β-O cleavage pathway would exist in the pyrolysis of α-OMe dimer **2**. A vinyl ether [2-(2-methoxyphenoxy)-1-(4-hydroxy-3-methoxyphenyl)ethene], which was also very labile under these pyrolysis conditions to give the β-ether cleaved product (guaiacol),[3] was detected in the pyrolyzate

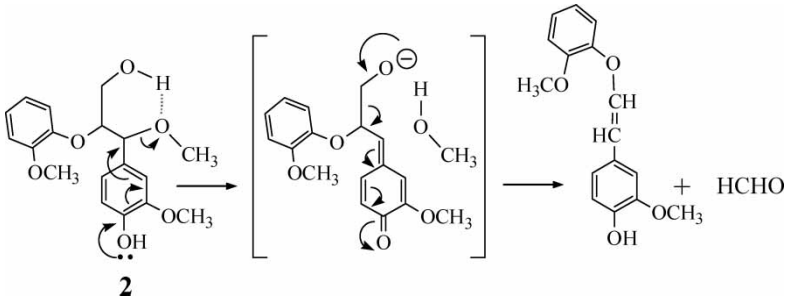


Figure 4. A proposed pyrolysis mechanism of dimer **2**.

of dimer **2** in 1.1% yield, although the yield is quite low due to further decomposition. Low 1-phenylpropene yield and detection of the vinyl ether indicate that some guaiacol form α-OMe dimer **2** is formed via vinyl ether intermediate produced through Cγ-elimination (pathway **b**). Consequently, the Cγ-methylation would increase the selectivity of the homolytic C$_\beta$-O cleavage via quinone methide (pathway **a**), while the Cα-methylation would increase the selectivity of the Cγ-elimination (pathway **b**).

Role of methylation on the selectivity between pathways **a** and **b** is explainable with hydrogen bonds between hydroxyl and methoxyl groups. In α-OMe dimer **2**, the hydrogen bond between methoxy oxygen and Cγ-OH hydrogen would be formed as shown in Fig. 4. Quinone methide formation from the hydrogen bonded structure would ionize the Cγ-OH to form the Cγ-O$^-$ with releasing methanol. From this ionized structure, Cγ-elimination is expected to proceed preferably. In guaicylglycerol-β-guaiacyl ether (**1**), both types of the hydrogen bonds are possible (Fig. 5), although their relative importance during pyrolysis is not known at the present. Type of the hydrogen bond would be important in the relative reactivity between pathways **a** and **b**. Type A hydrogen bond would enhance the Cγ-elimination

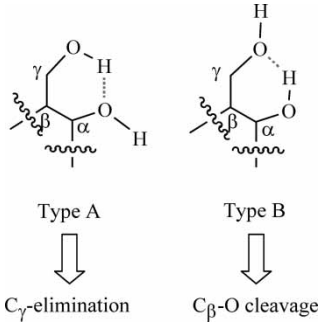


Figure 5. Role of hydrogen bonds on pyrolytic pathways of phenolic β-ether dimer.

(pathway **b**) as discussed for α-OMe dimer **2**, while the reactivity of the Cγ-elimination would be rather inhibited in type B hydrogen bond because the Cγ-oxygen is rather protonated during quinone methide formation from the hydrogen bonded structure.

CONCLUSIONS

Studies with the regiospecifically methylated dimers revealed that at least one hydroxyl group is required in the side-chain to maintain the high C_β-O cleavage reactivity of guaicylglycerol-β-guaiacyl ether. Intramolecular hydrogen bonds formed between the side-chain OH or OMe groups are proposed to explaine theses experimental results. Hydrogen bond types were also suggested to affect the reaction sequences between the Cγ-elimination followed by the C_β-O cleavage and the C_β-O homolysis via quinone methide intermediate.

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