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Effects of side-chain hydroxyl groups on pyrolytic β-ether cleavage of phenolic lignin model dimer

Abstract Effects of side chain hydroxyl groups on pyrolytic β-ether cleavage of phenolic model dimers were studied with various deoxygenated dimers under pyrolysis conditions of $N_2/400°C/1$ min. Although phenolic dimer with hydroxyl groups at the C_α- and C_γ-positions was much more reactive than the corresponding nonphenolic type, deoxygenation at the C_γ-position substantially reduced the reactivity up to the level of the nonphenolic type. These results are discussed with the cleavage mechanism via quinone methide intermediate formation, which is activated through intramolecular hydrogen bonds between C_α- and C_γ-hydroxyl groups.

Key words Lignin pyrolysis · Model compound · β-Ether cleavage · Effect of hydroxyl group

Introduction

The beta-ether linkage is an important structure in the pyrolytic depolymerization of lignin, because this structure, the most abundant structure in the lignin macromolecule, is reported to be cleaved effectively under pyrolysis conditions.[1–3] Studies using lignin model compounds indicated that the phenolic β-ether structure is more reactive than the nonphenolic type.[2,3] Although the content of phenolic structure is low in natural lignin,[4] chain depolymerization is expected via successive formation of the new phenolic structure through cleaving the phenolic end structure. Thus, the activation mechanism in the phenolic β-ether structure is especially important to understand and control the depolymerization behavior in lignin pyrolysis.

Several mechanisms including ionic (heterolytic) and homolytic mechanisms are proposed for the pyrolytic cleavage of the β-ether linkage. As for the ionic mechanism, retro-ene and oxirane mechanisms are proposed. Klein and Virk[5] proposed a six-centered retro-ene mechanism through kinetic analysis of the formation behavior of styrene and phenol from phenethyl phenyl ether, which has no substituent groups at the aromatic ring and side chain. Kislitsyn et al.[6] proposed an oxirane mechanism, in which β-ether is heterolytically cleaved by the attack of a C_α- or C_γ-hydroxyl group to the β-carbon. Brežný et al.[2] reported the several pyrolysis products from guaiacylglycerol-β-guaiacyl ether and explained their formation by an oxirane mechanism. As for the homolytic mechanism, homolytic C_β-O scission via benzyl radical is proposed for the pyrolytic cleavage of phenethyl phenyl ether.[7,8] Evans et al.[9] also proposed a modified homolytic mechanism assisted by the C_α-hydroxyl group. However, these mechanisms are still controversial because of the lack of supporting proof.

In solvent or under steam conditions, homolytic C_β-O cleavage via quinone methide intermediate is proposed by several groups. Sano's group[10–12] reported the several condensation products as proof of the quinone methide intermediate involved in the β-ether cleavage in the pulping reaction in a water–organic solvent mixture. Tanahashi et al.[13] also proposed a similar homolytic mechanism under steam explosion conditions. Kawamoto et al.[14] reported that the homolytic mechanism via the quinone methide intermediate is also important under pyrolysis conditions without solvent and steam environments. This conclusion was made from the relationship between reactivity and Hammett σ_p or the p-substituent parameter to reduce the bond dissociation energy of the aromatic O-CH_3 bond in pyrolysis of α- and α,β-diether model dimers and trimers with variously p-substituted C_α-phenyloxy groups. They also explained that higher reactivity of the phenolic form over the nonphenolic form is attributed to the easier formation of the quinone methide intermediate.

In this report, the roles of C_α- and C_γ-hydroxyl groups in the pyrolytic β-ether cleavage of a phenolic model dimer, studied with various deoxygenated dimers at 400°C, are presented.

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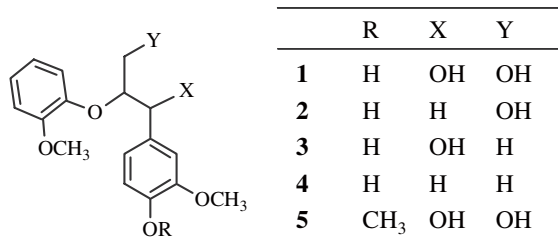e-mail: kawamoto@energy.kyoto-u.ac.jp

Fig. 1. Deoxygenated model dimers **1–5**

	R	X	Y
1	H	OH	OH
2	H	H	OH
3	H	OH	H
4	H	H	H
5	CH$_3$	OH	OH

Materials and methods

Pyrolysis products were separated by preparative thin-layer chromatography (TLC) on silica gel plates (Kieselgel 60 F$_{254}$, Merck). High performance liquid chromatography (HPLC) was carried out with a Shimadzu LC-10A under the following chromatographic conditions: column, STR ODS-II; flow rate, 0.7 ml/min; eluent, MeOH/H$_2$O = 30/70~100/0 (0~40 min), 100/0 (10 min); detection at 254 nm; 40°C). Proton nuclear 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.

Materials

Model compounds used in this study are shown in Fig. 1. 1-(4-Hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (guaicylglycerol-β-guaicyl ether, **1**) and 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (veratrylglycerol-β-guaiacyl ether, **5**) are described in a previous report.[3] α-Deoxy dimer, 3-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-propanol (**2**) was prepared by the modified procedure described by Freudenberg and Müller[15] and was identified by ^{1}H-NMR analysis of the acetate compared with the spectrum already reported.[16] γ-Deoxy dimer, 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-propanol (**3**) was prepared by the method described by Dimmel and Shepard.[17] α, γ-Dideoxy dimer, 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propane (dihydroeugenol-β-guaiacyl ether, **4**) was prepared according to the procedure described by McKague et al.[18] from β-bromodihydroeugenol and guaiacol, and was identified with the ^{1}H-NMR spectrum of the acetate compared with the spectrum already reported.[19]

Pyrolysis and product analysis

Pyrolysis of lignin model compounds was conducted with the experimental setup as previously reported,[3] which contained 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 tree-way tap. Model dimer (10 mg) was placed at the bottom of
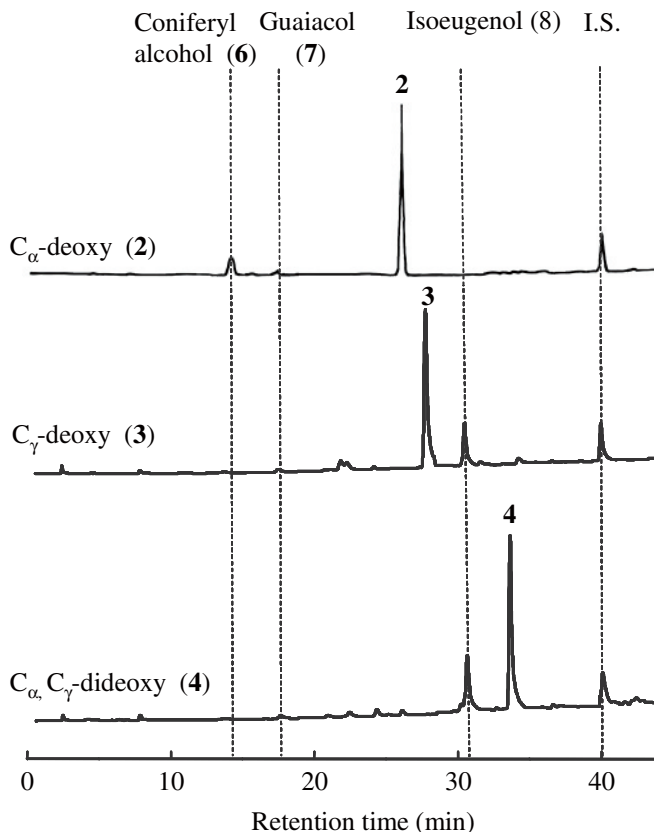

Fig. 2. Chromatograms from high performance liquid chromatography of the reaction mixtures obtained from dimers **2–4** under the pyrolysis conditions N$_2$/400°C/1 min

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) preheated at 400°C for 1 min. After pyrolysis, the flask was immediately cooled with air flow for 30 min and cold water, and then the reaction system was opened to release the gaseous products. The reaction mixture was extracted with tetrahydrofuran (THF) (5.0 ml × 2) and the combined solution was evaporated in vacuo to give the THF-soluble fraction. Products and the model dimer recovered in the THF-soluble fraction were quantified by HPLC with p-dibromobenzene as an internal standard. Coniferyl alcohol, isoeugenol, and guaiacol were also confirmed by ^{1}H-NMR spectra of the isolated compounds compared with those of the authentic compounds.

Results and discussion

Figure 2 shows the HPLC chromatograms of the pyrolysis mixtures obtained from deoxygenated model dimers **2–4** under the pyrolysis conditions (N$_2$/400°C/1 min). All model dimers gave similar types of products including 1-phenylpropnenes and guaiacol. Guaiacol is a product that indicates β-ether cleavage.

Table 1. Yields of some degradation products from dimers **1–5** under the pyrolysis conditions of $N_2/400°C/1\,min$

| Model compound	R	X	Y	Model compound reacted (%)	Products		
					Guaiacol	1-Phenylpropene	Vinyl ether
1	H	OH	OH	50.3	50.1	30.4[a]	Trace[d]
2	H	OH	H	7.9	3.5	1.1[b]	ND
3	H	H	OH	4.3	4.1	1.5[a]	ND
4	H	H	H	6.7	3.5	1.7[b]	ND
5	CH₃	OH	OH	8.4	3.1	0.5[c]	0.6[e]

ND, Not detected
[a] Coniferyl alcohol (**6**)
[b] Isoeugenol (**8**)
[c] 4-O-Methyl coniferyl alcohol (**9**)
[d] 2-(2-Methoxyphenoxy)-1-(4-hydroxy-3-methoxyphenyl)ethene (**10**)
[e] 2-(2-Methoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethene (**11**)

Table 1 summarizes the product yields from dimers **2–4**; the extent of reaction of the model dimer was determined by recovery of unreacted model dimer. The results for dimer **1** with hydroxyl groups at the C_α- and C_γ-positions and its nonphenolic type **5** are also included, both of which have been reported in the previous article.[3] Except for vinyl ether formation, product types were similar between deoxygenated dimers **2–4** and dimers **1** and **5**. However, the yields were quite different depending on the structure. Although phenolic dimer **1** is very reactive as indicated by the reacted model dimer (50.3%) and the product yields [guaiacol (50.1%) and 1-phenylpropene (coniferyl alcohol) (30.4%)], the reactivities of the deoxygenated dimers **2–4** are comparatively very low [reacted model dimers (4.3%–7.9%), guaiacol (3.5%–4.1%), and 1-phenylpropene (1.1%–1.7%)]. Interestingly, these reactivities are rather similar to that of nonphenolic dimer **5** [reacted model dimers (8.4%), guaiacol (3.1%) and 1-phenylpropene (4-O-methyl coniferyl alcohol) (0.5%)].

These results are very interesting in terms of the cleavage mechanism. As shown in Fig. 3, two types of reactions take place in the pyrolysis of β-ether model dimers, which include the C_β-O cleavage (pathway **a**) and C_γ-elimination to form vinyl ether (pathway **b**).[3] 1-Phenylpropenes are the products from pathway **a**. Phenolic vinyl ether structure was very reactive under the present pyrolysis conditions to form the β-ether cleaved products.[3] Therefore, there is little information about the reaction pathway **b** from the present results. However, low yields of the 1-phenylpropene derivatives as well as guaiacol from deoxygenated dimers **2–4** indicate that β-ether cleavage via pathway **a** is substantially suppressed in the deoxygenated structures to the level of the nonphenolic dimer **5**.

As already described, homolytic C_β-O cleavage is substantially activated in the quinone methide intermediate (Fig. 4),[14] probably due to lowering of the bond dissociation energy of the C_β-O bond in the quinone methide form.[20] Therefore, formation of the quinone methide intermediate is critical for the higher β-ether cleavage reactivity of the phenolic model dimer **1**. A C_α-hydroxyl group and p-hydroxylated aromatic ring are the important components in quinone methide formation from lignin-related compounds in solvent. However, low reactivity of the C_γ-
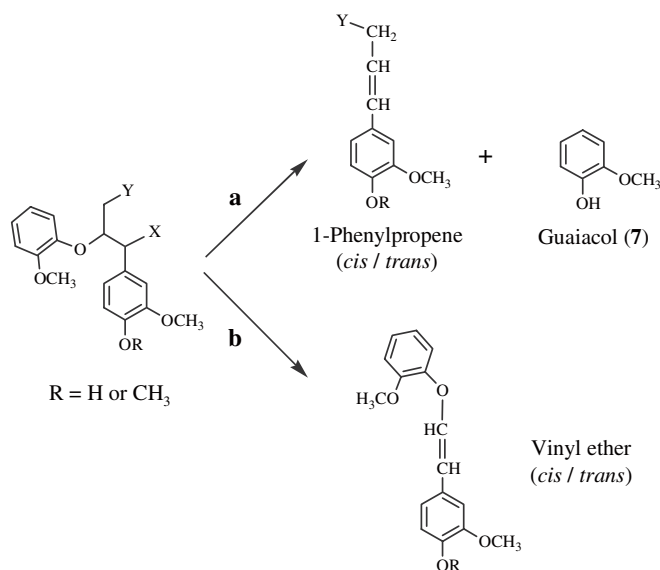
Fig. 3. Pyrolytic pathways of β-ether types of model dimers **1–5**

Quinonemethide   Cyclic transition states
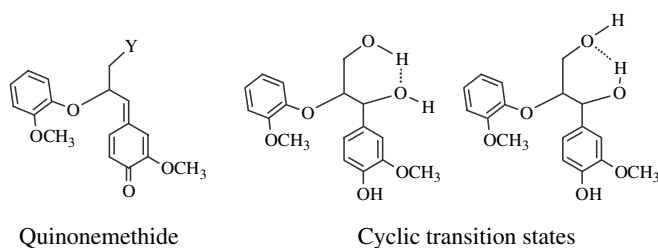
Fig. 4. Quinone methide intermediate and cyclic transition states

deoxygenated dimer **3**, which also has these components, indicates that quinone methide is not formed effectively during pyrolysis of dimer **3**. This leads to a very interesting conclusion that the C_γ-hydroxyl group plays an important role in quinone methide formation under pyrolysis conditions.

Unlike the reaction in solvent, pyrolysis conditions do not include the solvent stabilizing effects of polar or ionic species. Low reactivity of dimer **3** may be related to this characteristic nature of pyrolysis. Different pyrolytic

mechanisms were also indicated between dimers **1** and **3** in our preceding studies (Kawamoto et al. unpublished data). Although further study is necessary to confirm the hypothesis, high reactivity of dimer **1** for quinone methide formation is explainable with the stable cyclic transition state (Fig. 4) with hydrogen bonds between C_α- and C_γ-hydroxyl groups. A cyclic transition state mechanism is proposed for pyrolysis of β-hydroxy ketones,[21,22] β-hydroxy olefins,[23] and β,γ-unsaturated acids.[24,25] For example, thermal retrograde aldol condensation of some β-hydroxy ketones is reported to proceed much faster in structures that can form a cyclic transition state than in other similar β-hydroxy ketones.[21] The β-ether linkage in C_γ-deoxygenated dimer **3**, which cannot form these hydrogen bonds, is considered to proceed in direct homolytic C_β-O cleavage as like model dimers **2**, **4**, and **5**.

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