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NOTE

Effect of type of aromatic nucleus in lignin on the rate of the *β-O*-4 bond cleavage during alkaline pulping process

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Abstract Several C_6–C_3 and C_6–C_2-type dimeric non-phenolic *β-O*-4 lignin model compounds, whose aromatic nuclei consisting of the carbon skeleton and *β-O*-4 linkage are named the A- and B-rings, respectively, were treated under alkaline pulping conditions to examine whether or not the substitution of methoxyl group on the B-ring or of guaiacyl for syringyl A-ring accelerates the *β-O*-4 cleavage as a further study of our previous reports. It was suggested that either first or second substitution of methoxyl group on the B-ring accelerates the *β-O*-4 cleavage in both C_6–C_3 and C_6–C_2 compounds although the former compounds are more sensitive to the substitution than the latter, suggesting that the lack of the *γ*-hydroxymethyl group makes model compound insensitive to the substitution. It was confirmed that the substitution of guaiacyl for syringyl A-ring accelerates the *β-O*-4 cleavage in both C_6–C_3 and C_6–C_2 compounds with the degrees similar to each other regardless of the type of the B-ring. It was clarified that the leaving ability of the leaving B-ring phenoxides in the *β-O*-4 cleavage does not correlate well with the pK_a values of the conjugate acids of the phenoxides, which is not in accordance with the common property of a nucleophilic substitution reaction.

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Introduction

We have studied the effect of the structural differences in the aromatic nucleus and side-chain of *β-O*-4-type substructure in lignin on the rate of the *β-O*-4 bond cleavage during alkaline pulping process [1, 2], where the delignification is attained mainly by the reaction shown in Fig. 1. Dimeric non-phenolic *β-O*-4-type lignin model compounds employed in our previous reports are shown in Fig. 2, where two aromatic nuclei in each model compound are labeled as A- and B-rings and the abbreviation of the model compounds is based on the type [guaiacyl (G or G′) and syringyl (S)] of the A- and B-rings in this order. It was indicated that the *β-O*-4 bond cleavage of the *erythro* isomers of the C_6–C_3-type compounds is about 2–8 times as rapid as that of the corresponding *threo* isomers in the range of the employed reaction temperatures (130–170 °C) [1]. Although it had generally been accepted that the rate of the *erythro* isomer was about four times as large as that of the corresponding *threo* isomer [3–5], it was clarified that this rate difference is valid only for GG (Fig. 2) consisting only of guaiacyl nuclei and that the existence of syringyl nucleus deviates this rate difference from four times by accelerating the *β-O*-4 bond cleavage of each isomer with different degrees. It was also shown that the effect of the presence of syringyl nucleus as the B-ring is much greater than that as the A-ring. It was confirmed, thus, that the structural difference in the aromatic nucleus of *β-O*-4 substructure affects the rate of the *β-O*-4 bond cleavage conjunctly with that in the side-chain [1].
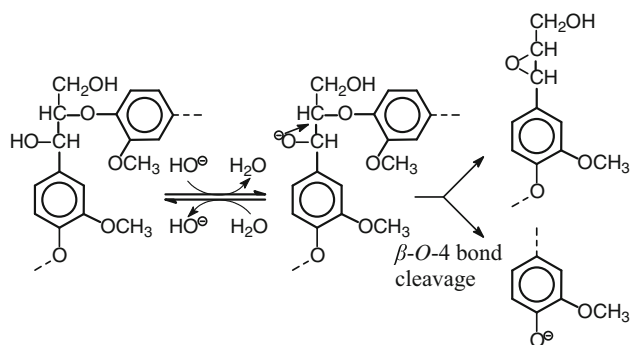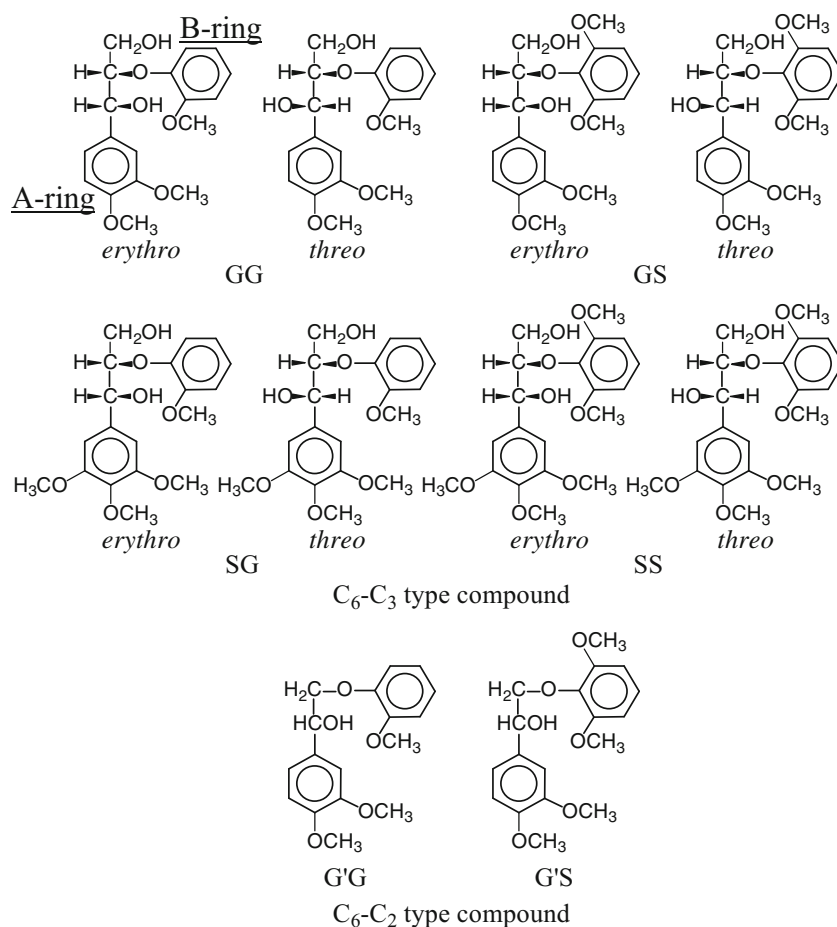
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Fig. 1 The general mechanism for the β-O-4 bond cleavage of non-phenolic lignin substructures during alkaline pulping process

Then, dimeric non-phenolic β-O-4-type lignin model compounds without the γ-hydroxymethyl group (C_6–C_2 type in Fig. 2) were employed to eliminate the effect of the presence of the γ-hydroxymethyl group and consequent diastereomerism and to examine the effect of the structural difference in the aromatic nucleus on the rate of the β-O-4 bond cleavage independently on that in the side-chain [2]. It was shown that the rates of the β-O-4 bond cleavage are clearly different between G'G and G'S (Fig. 2)

accompanying the structural difference in the aromatic nucleus (the substitution of the guaiacyl for syringyl B-ring) although the difference between the rates is smaller than that between GG and GS (Fig. 2) carrying the γ-hydroxymethyl group. It was also indicated that the rate of G'G or G'S is in between those of the *erythro* and *threo* isomers of GG or GS, respectively. These results confirmed that the structural difference in the aromatic nucleus affects the rate of the β-O-4 bond cleavage independently on that in the side-chain.

In this report, the effect of the structural difference in the aromatic nucleus was further examined. Because the effect of the presence of syringyl nucleus as the B-ring is much greater than that as the A-ring (the rate: GG $\ll$ GS, G'G $\ll$ G'S, GG < SG) [1, 2], it is assumed that the presence of methoxyl group on the B-ring should significantly affect the reaction rate. To discuss this assumption, dimeric non-phenolic β-O-4-type lignin model compounds with the *p*-hydroxylphenyl (H) B-ring, GH and G'H (Fig. 3), were treated under alkaline pulping conditions. Furthermore, other C_6–C_2-type compounds with the syringyl A-ring, S'H, S'G, and S'S (Fig. 3), were also treated to confirm the effect of the presence of the syringyl

Fig. 2 Chemical structure of the dimeric non-phenolic β-O-4-type lignin model compounds employed in our previous reports [1, 2]. GG, 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol; GS, 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol; SG, 2-(2-methoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)propane-1,3-diol; SS, 2-(2,6-dimethoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)propane-1,3-diol; G'G, 2-(2-methoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethanol; G'S, 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethanol
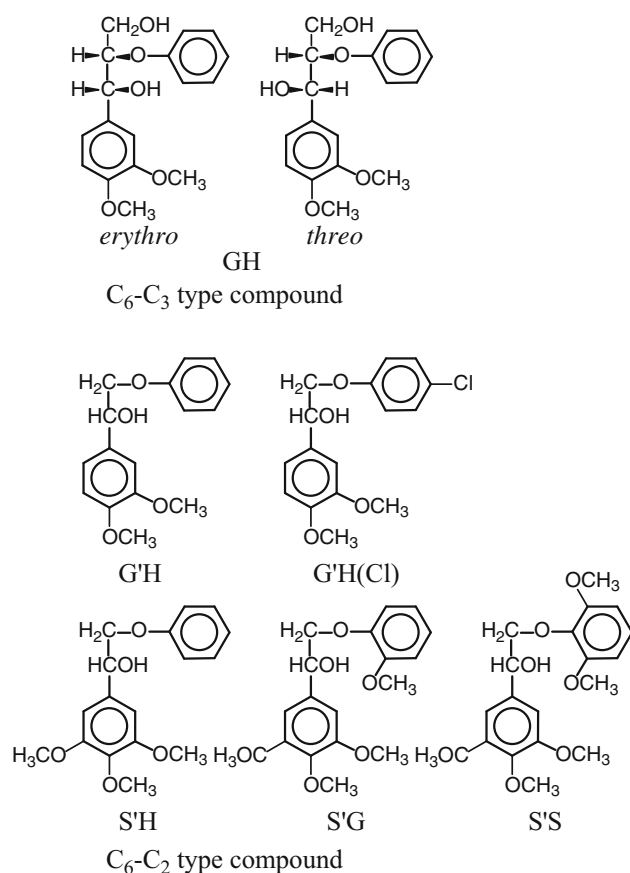
Fig. 3 Chemical structure of dimeric non-phenolic β-*O*-4-type lignin model compounds employed in this report. GH, 1-(3,4-dimethoxyphenyl)-2-phenoxypropane-1,3-diol; G′H, 1-(3,4-dimethoxyphenyl)-2-phenoxyethanol; G′H(Cl), 2-(4-chlorophenoxy)-1-(3,4-dimethoxyphenyl)ethanol; S′H, 1-(3,4,5-trimethoxyphenyl)-2-phenoxyethanol; S′G, 2-(2-methoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)ethanol; S′S, 2-(2,6-dimethoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)ethanol

A-ring is also less greater than that of the syringyl B-ring in the reaction of C_6–C_2-type compound. Another model compound with the *p*-chlorophenyl (H(Cl)) B-ring, G′H(Cl) (Fig. 3), was also employed as that consisting of a B-ring with the high-leaving ability in the reaction of the β-*O*-4 bond cleavage. The lignin model compounds employed in this report are shown in Fig. 3.

Materials and methods

Materials

All the chemicals used in this report were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) or Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Water was deionized and degassed before use. All the dimeric lignin mode compounds employed in this report were synthesized in accordance with the method of Adler et al. [6]. To confirm the structures and purities, the ^{1}H- and ^{13}C-NMR

spectra (JNM-A500, 500 MHz, JEOL Ltd., Tokyo, Japan) of these model compounds were recorded using acetone-d_6 and aliquots of D_2O as solvents. The mass spectra of these model compounds were also analyzed using GC2010/PARVUM2 (GC/MS), Shimadzu Co., Kyoto, Japan.

Methods

All the systems in the reaction of GH were almost the same as those described in our previous report [1]. Those of the others were almost the same as those described in our previous report [2]. The conditions were as follows: concentration of NaOH: 1.0 mol/l, initial concentration of model compound: 1.2 mmol/l (GH, G′H, S′H, S′G, or S′S); 0.6 mmol/l (G′H(Cl)), temperature: three points among 130, 140, 150, 160, and 170 °C.

In the work-up procedure for all the compounds except G′H(Cl), the autoclave was cooled in an ice water bath and the content was neutralized with acetic acid. Methanol (2.0 ml) containing an internal standard compound, 4-chlorophenol, was added to the autoclave. After filtration, the mixture was directly analyzed by HPLC (LC-10A, Shimadzu Co., Kyoto, Japan) equipped with an SPD-M10A detector (280 nm, Shimadzu Co.) to quantify the residual lignin model compound and phenolic compound liberated from the B-ring of each model compound, phenol (from GH, G′H, or S′H), 2-methoxyphenol (guaiacol, from S′G), or 2,6-dimethoxyphenol (syringol, from S′S), accompanying the β-*O*-4 bond cleavage.

In the work-up procedure of G′H(Cl), the method was almost the same as those described in our previous report [2]. As the phenolic compound liberated from the B-ring, 4-chlorophenol was quantified using 3,4-dimethoxytoluene as an internal standard compound. An extraction with diethyl ether was additionally conducted.

The conditions for the HPLC analysis in this report were as follows: column: Luna 5u C18(2) 100 A (150 mm × 4.6 mm, Phenomenex Inc., Torrance, CA, USA); oven temperature: 40 °C; flow rate: 1.0 ml/min; solvent system: gradient CH_3OH/H_2O (v/v) from 25/75 to 60/40 for 30 min and maintained for 2.5 min, gradient to 90/10 immediately and maintained for 12.5 min, total time: 45 min.

Results and discussion

General description

Organic co-solvents have always been used in alkaline pulping reactions of dimeric non-phenolic β-*O*-4-type lignin model compounds. It was reported, however, that organic co-solvents affect the rate of the β-*O*-4 bond

cleavage and that the effect is greater in the reaction of a C_6–C_2-type compound than in that of a C_6–C_3-type compound [6]. Therefore, no organic co-solvent was used in this and our previous reports [1, 2]. Although each C_6–C_2-type model compound did not completely dissolve in the
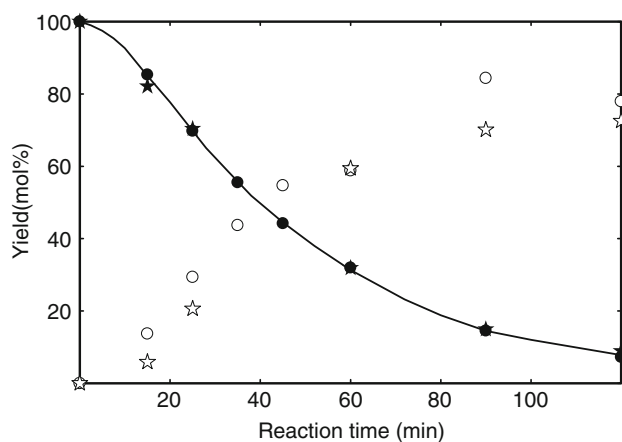

Fig. 4 Change in the yields of S′G and guaiacol, when S′G was treated at 150 °C. *Filled circle*, *filled star* S′G, *open circle*, *open star* guaiacol, *filled circle*, *open circle* 1st trial, *filled star*, *open star* 2nd trial
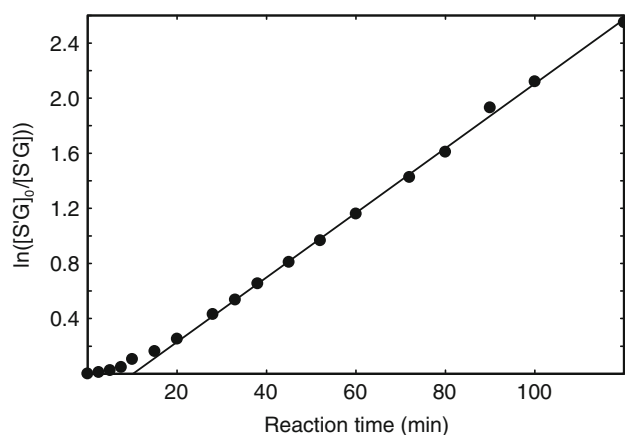

Fig. 5 Logarithmic plot of the disappearance of S′G, when S′G was treated at 150 °C. [S′G]$_0$: initial yield of S′G, [S′G]: yield of S′G

NaOH solution at room temperature, the disappearance was well approximated to a pseudo-first-order reaction after a certain period of the reaction (the initial stage), and hence, the pseudo-first-order reaction rate constant k_{obs} could be obtained in each compound [2]. This phenomenon suggests that each compound completely dissolved after the initial stage. Figure 4 shows the disappearance of S′G and formation of guaiacol in the reaction of S′G at 150 °C. Figure 5 shows the logarithmic plot of the disappearance of S′G at 150 °C. The sum of the yields of S′G and guaiacol was always almost 100 %, which indicates that the disappearance of S′G accompanies the *β-O*-4 bond cleavage almost quantitatively. The disappearances of all the other model compounds and formations of the phenol derivatives originating from their B-rings were similar to those of S′G.

Table 1 lists the value of k_{obs} observed in this report. Table 2 lists the Arrhenius' activation energy E_a and frequency factor A obtained from the Arrhenius' plot prepared from the value of k_{obs}. The rate constants k at 130, 140, 150, 160, and 170 °C listed in Table 2 were calculated on the basis of the values of E_a and A. As reference, Table 3 lists the value of E_a, A, and k of the model compounds employed in our previous reports [1, 2]. Table 4 lists the ratio of the k values between specific two compounds to compare their reaction rates.

Reaction of GH and the comparison with the other C_6–C_3-type compounds

The *β-O*-4 bond cleavage of the *erythro* isomer of GH was more rapid than that of the *threo* isomer at any temperature (Table 2), which is in accordance with all the other C_6–C_3-type compounds examined in our previous report [1]. The ratio of $k_{GH-erythro}/k_{GH-threo}$ decreases from 3.7 (130 °C) to 3.1 (170 °C) with increasing temperature (Table 4). The ratio is slightly smaller than the generally accepted value '4', which was confirmed to be valid only for GG consisting only of guaiacyl nuclei in our previous report [1]. Contrarily, the ratio varies in between 2.7 and 7.9, when model compound consists of a syringyl nucleus [1].

Table 1 List of the pseudo-first-order reaction rate constants (k_{obs}) observed in this report

	GH		G′H	S′H	S′G	S′S	G′H(Cl)
	erythro	*threo*					
k_{obs}^a							
130 °C	–	–	–	–	–	–	–
140 °C	–	–	–	–	–	28.3	–
150 °C	8.78	2.75	8.34	11.5	23.4	58.9	29.9
160 °C	21.1	6.35	19.3	24.3	51.0	118	69.9
170 °C	48.8	15.7	38.7	52.7	103	–	–

^{a} Unit: $\times 10^{-3}$ min^{-1}

Table 2 List of the Arrhenius' activation energies (E_a), Arrhenius' frequency factors (A), and reaction rate constants (k) obtained in this report

	GH		G'H	S'H	S'G	S'S	G'H(Cl)
	erythro	*threo*					
E_a^a	133	140	120	118	117	106	–
A^b	265	509	5.57	4.96	6.12	0.730	–
k^c							
130 °C	1.34	0.360	1.56	2.14	4.52	13.2	–
140 °C	3.51	0.985	3.70	5.04	10.5	28.3	–
150 °C	8.80	2.58	8.46	11.4	23.5	58.8	–
160 °C	21.1	6.48	18.6	24.8	50.5	118	–
170 °C	48.8	15.6	39.5	52.2	105	229	–

[a] Unit: $\times kJ\ mol^{-1}$

[b] Unit: $\times 10^{12}\ min^{-1}$

[c] Unit: $\times 10^{-3}\ min^{-1}$

Table 3 List of the Arrhenius' activation energies (E_a), Arrhenius' frequency factors (A), and reaction rate constants (k) obtained in our previous reports [1, 2]

	GG		GS		SG		SS		G'G	G'S
	erythro	*threo*	*erythro*	*threo*	*erythro*	*threo*	*erythro*	*threo*		
E_a^a	130	133	108	121	121	129	88.6	129	101	98.3
A^b	294	166	2.33	16.4[d]	30.2	60.5	0.0108	127	0.0609	0.0576
k^c										
130 °C	4.63	1.07	20.9	3.51	6.80	1.31	34.7	4.37	5.52	10.6
140 °C	11.8	2.79	45.8	8.42	16.3	3.29	65.8	11.1	11.4	21.5
150 °C	28.8	6.96	96.7	19.4	37.5	7.90	121	26.9[d]	22.8	42.1
160 °C	67.4	16.7	197	42.8	82.9	18.2	217	62.6	44.2	80.2
170 °C	152	38.4	389	91.5	177	40.5	378	140	83.1	148

For GG, GS, SG, and SS [1], for G'G and G'S [2]

[a] Unit: $\times kJ\ mol^{-1}$

[b] Unit: $\times 10^{12}\ min^{-1}$

[c] Unit: $\times 10^{-3}\ min^{-1}$

[d] These data are different from those listed in the reference no. 1, where the wrong data were listed

The k values of GH, GG, and GS were in the order of: $k_{GH} < k_{GG} < k_{GS}$ in the comparison of either the *erythro* or *threo* isomers at any temperature (Table 2), indicating that the presence of methoxyl group on the B-ring accelerates the β-O-4 bond cleavage. The ratios of k_{GG}/k_{GH} and k_{GS}/k_{GH}, which are indices of the effect of the methoxyl group substitution on the B-ring in the reaction of the C_6–C_3-type model compounds with guaiacyl A-ring, decrease with increasing temperature and are in between 3.5 (130 °C) and 3.1 (170 °C) and in between 15.6 (130 °C) and 8.0 (170 °C), respectively, in the *erythro* isomers (Table 4). In the *threo* isomers, these are in between 3.0 (130 °C) and 2.5 (170 °C) and in between 9.8 (130 °C) and 5.9 (170 °C), respectively (Table 4). Because the ratio of k_{GS}/k_{GH} is always more than two times of k_{GG}/k_{GH}, it is suggested that the second substitution of methoxyl group on the B-ring has an effect greater than

the first substitution and that the *erythro* isomers are more sensitive to either the first or second substitution than the corresponding *threo* isomers.

Reaction of C_6–C_2-type compounds

The k values of the C_6–C_2-type compounds employed in this and our previous reports [2] except G'H(Cl) were in the order of: $k_{G'H} < k_{S'H} < k_{G'G} < k_{S'G} < k_{G'S} < k_{S'S}$ at any temperature (Table 2), indicating that the methoxyl group substitution on either the A- or B-ring accelerates the β-O-4 bond cleavage and that the effect of the substitution on the B-ring is greater than that on the A-ring. These results are of the same tendency as those of the C_6–C_3-type compounds, which confirms that the type of aromatic nucleus affects the rate of the β-O-4 bond cleavage in the absence of the γ-hydroxymethyl group. However, the

Table 4 List of the ratios between various k values for the comparisons described in the text

	$k_{GH\text{-}erythro}/$ $k_{GH\text{-}threo}$		$k_{GG\text{-}erythro}/$ $k_{GG\text{-}threo}$		$k_{GS\text{-}erythro}/$ $k_{GS\text{-}threo}$		$k_{SG\text{-}erythro}/$ $k_{SG\text{-}threo}$		$k_{SS\text{-}erythro}/$ $k_{SS\text{-}threo}$	
130 °C	3.7		4.3		6.0		5.2		7.9	
140 °C	3.6		4.2		5.4		5.0		5.9	
150 °C	3.4		4.1		5.0		4.7		4.5	
160 °C	3.3		4.0		4.6		4.6		3.5	
170 °C	3.1		4.0		4.3		4.4		2.7	
	k_{GG}/k_{GH}		k_{GS}/k_{GH}		k_{SS}/k_{SG}		k_{SG}/k_{GG}		k_{SS}/k_{GS}	
	erythro	threo	erythro	threo	erythro	threo	erythro	threo	erythro	threo
130 °C	3.5	3.5	15.6	9.8	5.1	3.3	1.5	1.2	1.7	1.2
140 °C	3.4	2.8	13.0	8.5	4.0	3.4	1.4	1.2	1.4	1.3
150 °C	3.3	2.7	11.0	7.5	3.2	3.4	1.3	1.1	1.3	1.4
160 °C	3.2	2.6	9.3	6.6	2.6	3.4	1.2	1.1	1.1	1.5
170 °C	3.1	2.5	8.0	5.9	2.1	3.5	1.2	1.1	1.0	1.5
	$k_{G'G}/$ $k_{G'H}$		$k_{G'S}/$ $k_{G'H}$		$k_{S'G}/$ $k_{S'H}$		$k_{S'S}/$ $k_{S'H}$		$k_{S'S}/$ $k_{S'G}$	
130 °C	3.5		6.7		2.1		6.2		2.9	
140 °C	3.1		5.9		2.1		5.6		2.7	
150 °C	2.7		5.2		2.1		5.2		2.5	
160 °C	2.4		4.6		2.0		4.8		2.3	
170 °C	2.1		4.1		2.0		4.4		2.2	
	$k_{S'H}/$ $k_{G'H}$		$k_{S'G}/$ $k_{G'G}$		$k_{S'S}/$ $k_{G'S}$					
130 °C	1.4		0.8		1.3					
140 °C	1.4		0.9		1.3					
150 °C	1.3		1.0		1.3					
160 °C	1.3		1.1		1.4					
170 °C	1.3		1.3		1.4					

degree of the effects is different between the C_6–C_3 and C_6–C_2-type compounds, and hence, will be discussed in the following sections.

In addition, when the k values of the C_6–C_3 and C_6–C_2-type compounds with the consistent aromatic nuclei were compared, the order was: the *threo* isomer of C_6–C_3-type compound < C_6–C_2-type compound < the *erythro* isomer of C_6–C_3-type compound in most cases (Tables 2, 3). A possible explanation was presented in our previous report [2].

Effect of the type of aromatic B-ring

When the k values of the C_6–C_2-type compounds with guaiacyl A-ring, G′H, G′G, and G′S, were compared to examine the effect of the type of B-ring of the compounds, the order was: $k_{G'H} < k_{G'G} < k_{G'S}$ at any temperature (Tables 2 and 3). The ratios of $k_{G'G}/k_{G'H}$ and $k_{G'S}/k_{G'H}$, which are indices of the effect of the methoxyl group substitution on the B-ring in the reaction of the C_6–C_2-type compounds with guaiacyl A-ring, decrease with increasing temperature and are in between 3.5 (130 °C) and 2.1 (170 °C) and in between 6.7 (130 °C) and 4.1 (170 °C), respectively (Table 4). Because the ratio of $k_{G'S}/k_{G'H}$ is about two times of $k_{G'G}/k_{G'H}$, it is suggested that the first substitution of methoxyl group on the B-ring has an effect similar to the second substitution. This result is different from that obtained in the reaction of the C_6–C_3-type compounds described above. Since the ratios of k_{GG}/k_{GH} and k_{GS}/k_{GH} in both the *erythro* and *threo* isomers are commonly larger than those of $k_{G'G}/k_{G'H}$ and $k_{G'S}/k_{G'H}$, respectively, it is suggested that the presence of the γ-hydroxymethyl group makes model compound sensitive to either the first or second substitution.

When the k values of the C_6–C_2-type compounds with syringyl A-ring, S′H, S′G, and S′S, were compared, the

order was: $k_{S'H} < k_{S'G} < k_{S'S}$ at any temperature (Table 2). The ratios of $k_{S'G}/k_{S'H}$ and $k_{S'S}/k_{S'H}$, which are indices of the effect of the methoxyl group substitution on the B-ring in the reaction of the C_6–C_2-type compounds with syringyl A-ring, decrease with increasing temperature and are in between 2.1 (130 °C) and 2.0 (170 °C) and in between 6.2 (130 °C) and 4.4 (170 °C), respectively (Table 4). The $k_{S'S}/k_{S'H}$ can be stated to be more than two times of $k_{S'G}/k_{S'H}$, which is not the same as the above-described relationship between $k_{G'G}/k_{G'H}$ and $k_{G'S}/k_{G'H}$ and suggests that the second substitution of methoxyl group affects more greatly that the first substitution. The ratios of $k_{S'G}/k_{S'H}$ and $k_{S'S}/k_{S'H}$ are mostly smaller than $k_{G'G}/k_{G'H}$ and $k_{G'S}/k_{G'H}$, respectively. It is indicated, therefore, that the effect of the substitution of methoxyl group on the B-ring is less great in the reaction of the C_6–C_2-type compounds with syringyl A-ring than in that with guanacyl A-ring. The ratio of $k_{S'S}/k_{S'G}$, which is an index of the effect of the substitution of guaiacyl for syringyl B-ring in the reaction of the C_6–C_2-type compounds with syringyl A-ring, decreases with increasing temperature and is in between 2.9 (130 °C) and 2.2 (170 °C), while the ratio of the *erythro* and *threo* isomers of the corresponding C_6–C_3-type compounds, k_{SS}/k_{SG} (an index of the effect of the substitution of guaiacyl for syringyl B-ring in the reaction of the C_6–C_3-type compounds with syringyl A-ring), is in between 5.1 (130 °C) and 2.1 (170 °C) and in between 3.3 (130 °C) and 3.5 (170 °C), respectively. Therefore, the ratios of k_{SS}/k_{SG} are commonly larger than those of $k_{S'S}/k_{S'G}$ at most temperatures, which shows that the presence of the γ-hydroxymethyl group makes model compound sensitive to the substitution of guaiacyl for syringyl B-ring in the reaction of the model compounds with syringyl A-ring. This is the same tendency as the relationship between the model compounds with guaiacyl A-ring (k_{GS}/k_{GG} and $k_{G'S}/k_{G'G}$).

Based on the above discussion, it is suggested that either the first or second substitution of methoxyl group on the B-ring accelerates the β-O-4 bond cleavage in the reaction of both C_6–C_3 and C_6–C_2 compounds and that the lack of the γ-hydroxymethyl group makes model compound insensitive to the variation of the type of B-ring.

Effect of the type of aromatic A-ring

When a pair of the k values of G′H and S′H, of G′G and S′G, or of G′S and S′S was compared, the order was: $k_{G'H} < k_{S'H}$, $k_{G'G} < k_{S'G}$, or $k_{G'S} < k_{S'S}$, respectively, at all the temperatures except that the order was $k_{S'G} < k_{G'G}$ at 130 °C (Table 2). It should be noted that the reactions of G′G and S′G were not actually run at 130 °C but the calculations on the basis of the Arrhenius' parameters yielded the values of $k_{G'G}$ and $k_{S'G}$ at 130 °C. The ratios of $k_{S'H}/k_{G'H}$, which is an index of the effect of the substitution of

guaiacyl for syringyl A-ring in the reaction of the C_6–C_2-type compounds with *p*-hydroxylphenyl B-ring, decrease with increasing temperature and are in between 1.4 (130 °C) and 1.3 (170 °C) (Table 4). Those of $k_{S'G}/k_{G'G}$ and $k_{S'S}/k_{G'S}$, which are indices analogous to the above, increase with increasing temperature and are in between 0.8 (130 °C) and 1.3 (170 °C) and in between 1.3 (130 °C) and 1.4 (170 °C), respectively. It is indicated, similarly to the phenomena observed in the reaction of the C_6–C_3-type compounds [1], that the substitution of guaiacyl for syringyl A-ring accelerates the rate of the β-O-4 bond cleavage in most cases regardless of the type of aromatic B-ring.

The ratios of k_{SG}/k_{GG}, which is an index of the effect of the substitution of guaiacyl for syringyl A-ring in the reaction of the C_6–C_3-type compounds with guaiacyl B-ring, decrease with increasing temperature and are in between 1.5 (130 °C) and 1.2 (170 °C) in the *erythro* isomers and in between 1.2 (130 °C) and 1.1 (170 °C) in the *threo* isomers (Table 4). The ratios of k_{SS}/k_{GS}, which is an index analogous to the above, in the *erythro* isomers decrease with increasing temperature and are in between 1.7 (130 °C) and 1.0 (170 °C), while these increase with increasing temperature and are in between 1.2 (130 °C) and 1.5 (170 °C) in the *threo* isomers. It is suggested by the comparisons between $k_{S'G}/k_{G'G}$ and k_{SG}/k_{GG} and between $k_{S'S}/k_{G'S}$ and k_{SS}/k_{GS} that the lack of the γ-hydroxymethyl group does not largely affect the effect of the substitution of guaiacyl for syringyl A-ring on the rate of the β-O-4 bond cleavage, which is in contrast to the observation in the effect of the substitution of guaiacyl for syringyl B-ring.

Reaction of G′H(Cl) and the comparison with the other C_6–C_2-type compounds

The leaving ability of a leaving group is an important rate-determining factor in a nucleophilic substitution reaction. It is generally known that the leaving ability of a leaving group correlates well with the pK_a value of the conjugate acid of the leaving group and increases with decreasing the pK_a value [7]. Because the second step of the β-O-4 bond cleavage is an intramolecular nucleophilic substitution reaction (Fig. 1), the rates of the β-O-4 bond cleavage of G′H, G′G, and G′S possibly correlate with the pK_a values of the conjugate acids of the leaving groups, phenol, guaiacol, and syringol, respectively. The pK_a values of these compounds were reported to be 9.99 [8], 9.93 [9], and 9.98 [9], respectively. On the basis of these values, the rate constants can be in the order of: $k_{G'H} \leq k_{G'S} \leq k_{G'G}$, although the pK_a values are similar and the rate difference may be small. However, this estimation is inconsistent with the obtained results. It should be examined, thus, whether or not the rate of the β-O-4 bond cleavage of a dimeric

non-phenolic β-O-4-type lignin model compound is rapid when the pK_a value of the conjugate acid of the leaving group is low. G′H(Cl) was employed and treated under the alkaline pulping conditions, because the pK_a value of the conjugate acid of the leaving group of G′H(Cl), 4-chlorophenol, is relatively low 9.38 [10].

The k values of G′H, G′G, G′S, and G′H(Cl) were in the order of: $k_{G'H} < k_{G'G} < k_{G'H(Cl)} < k_{G'S}$ at any temperature (Table 1). It was clarified, therefore, that the rates of the β-O-4 bond cleavage of the model compounds do not correlate with the pK_a values of the conjugate acids of the leaving B-ring phenoxides, phenoxide, guaiacoxide, syringoxide, and 4-chlorophenoxide, respectively. It could be stated, however, that this correlation exists in the reactions between G′H and G′H(Cl) carrying no *ortho*-substituted methoxyl group on the B-ring. This result is probably attributed to the fact that G′G and G′S have the *ortho*-substituted methoxyl group(s) sterically affecting the reaction rates.

Conclusions

It was suggested that either the first or second substitution of methoxyl group on the B-ring accelerates the β-O-4 bond cleavage in the reaction of both C_6–C_3 and C_6–C_2 compounds and that the lack of the γ-hydroxymethyl group makes model compound insensitive to the variation of the type of B-ring. It was confirmed that the substitution of guaiacyl for syringyl A-ring accelerates the β-O-4 bond cleavage even in the reaction of the C_6–C_2-type compounds. It was also indicated that the leaving abilities of the leaving B-ring phenoxides are not in accordance with those estimated from the pK_a values of their conjugate acids and that syringoxide has an especially high leaving ability.

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