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### Delignification Mechanism During High-Boiling Solvent Pulping. IV. Effect of a Reducing Sugar on the Degradation of Guaiacylglycerol- $\beta$ -guaiacyl Ether

Takao Kishimoto<sup>a</sup>; Yoshihiro Sano<sup>a</sup>

<sup>a</sup> Laboratory of Wood Chemistry, Research Group of Bioorganic Chemistry, Division of Applied Bioscience, Graduate School of Agriculture, Hokkaido University, Sapporo, Japan

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## Delignification Mechanism During High-Boiling Solvent Pulping. IV. Effect of a Reducing Sugar on the Degradation of Guaiacylglycerol- $\beta$ -guaiacyl Ether

Takao Kishimoto\* and Yoshihiro Sano

Laboratory of Wood Chemistry,  
Research Group of Bioorganic Chemistry,  
Division of Applied Bioscience,  
Graduate School of Agriculture, Hokkaido University,  
Sapporo, Japan

### ABSTRACT

A phenolic  $\beta$ -O-4 type lignin model compound, guaiacylglycerol- $\beta$ -guaiacyl ether was treated with 70 wt% aqueous 1,3-butanediol solution in the presence of glucose at 160–200°C to investigate the effect of reducing sugars on the degradation of lignin during high-boiling solvent (HBS) pulping. Addition of glucose increased the formation of guaiacol, coniferyl alcohol, and its  $\gamma$ -ethers, and

\*Correspondence: Takao Kishimoto, Laboratory of Wood Chemistry, Research Group of Bioorganic Chemistry, Division of Applied Bioscience, Graduate School of Agriculture, Hokkaido University, Sapporo 060-8589, Japan; E-mail: takao@for.agr.hokudai.ac.jp.



decreased the formation of radical coupling compounds dramatically. These results suggest that reducing sugars may stabilize phenoxy radicals formed by homolysis of phenolic  $\beta$ -ethers. The kinetic studies also revealed that the disappearance of the  $\beta$ -ether model compound was enhanced substantially by the presence of glucose, which suggests that in addition to homolysis of the  $\beta$ -ether, a reducing sugar-assisted  $\beta$ -ether cleavage may be involved under the conditions used.

## INTRODUCTION

High-boiling solvent (HBS) pulping is organosolv pulping based on aqueous high-boiling solvents such as aqueous 1,3-butanediol (b.p. 208°C) and 1,4-butanediol (b.p. 232°C). We showed that aqueous HBS were very effective for delignifying both hardwoods and softwoods, even without an acid catalyst, at 200°C and 220°C.<sup>[1]</sup> The solvents can be reused repeatedly after removing high molecular weight lignin from the spent liquor by precipitation. The recovered lignin can be used for many purposes such as a source of epoxy resin.

In this study, the delignification mechanism during HBS pulping was investigated by using a phenolic  $\beta$ -O-4 type lignin model compound, guaiacylglycerol- $\beta$ -guaiacyl ether (**1**, Fig. 1). Guaiacol, coniferyl alcohol and several radical coupling products were isolated as reaction products by heating compound **1** in aqueous 1,3- or 1,4-butanediol solutions at 160–220°C. Acidolysis products such as Hibbert's ketones were not detected as reaction products. Thus, we proposed that the phenolic  $\beta$ -aryl ether linkages in lignin were cleaved homolytically via quinone methide intermediates under HBS pulping conditions as shown in Fig. 2. Recombination of the phenoxy radicals which are formed could occur to some extent. It was also reported that homolysis of the  $\beta$ -ether

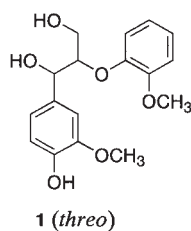


Figure 1. Model compound **1** used in this study.



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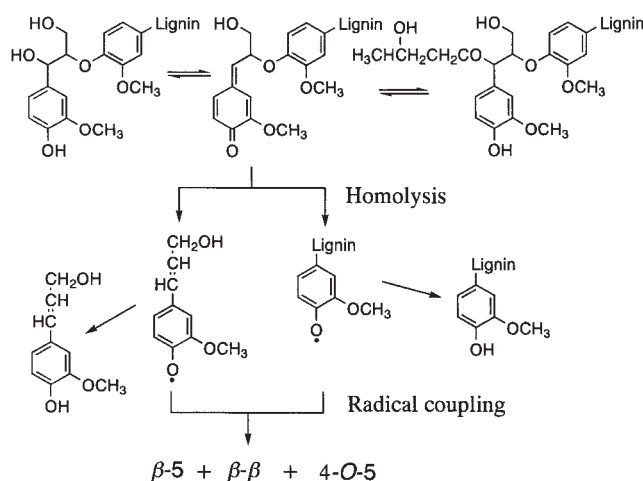


Figure 2. Homolysis of phenolic  $\beta$ -aryl ether during HBS pulping.

followed pseudo-first order kinetics with an activation energy of 98.3 kJ/mol.<sup>[2,3]</sup>

However, Kajimoto and Sano reported that recovered solvents (RHBS) from spent liquors were better pulping solvents than a fresh solvent.<sup>[4]</sup> They cooked todo fir (*Abies sachalinensis* MAST) in 70% recovered aqueous butanediol solutions at 220°C, and showed that the delignification rate was 1.5 times greater than that with a fresh solvent, even though the RHBS contained soluble lignin, sugars, and their modified compounds. They also found that the addition of a reducing sugar to the fresh solvent accelerated the delignification rate dramatically. The effects of the RHBS were attributed to reducing sugars they contain. The possibility of reducing sugar-assisted reactions in addition to homolytic cleavage of the phenolic  $\beta$ -aryl ethers were considered. Other interesting results have been reported by Li and others in connection with the reaction mechanisms of phenolic  $\beta$ -ether cleavage.<sup>[5]</sup> They treated compound **1** under sulfite pulping conditions (160°C, 2 h), but failed to detect coniferyl alcohol or its sulfonates. Homolytic cleavage of the  $\beta$ -aryl ether bond seemed to be inhibited by the addition of sulfite. The results suggested that additives may alter the reaction mechanisms of phenolic  $\beta$ -aryl ether cleavage to some extent.

In this study, guaiacylglycerol- $\beta$ -guaiacyl ether (**1**) was treated with 70 wt% aqueous 1,3-butanediol solution in the presence and absence of glucose in order to elucidate the effects of reducing sugars on the



degradation of compound **1**. Reaction products were analyzed by gas chromatography and mass spectroscopy. Gel permeation chromatography was also conducted to analyze the formation of radical coupling products.

## EXPERIMENTAL

### Reaction of Guaiacylglycerol- $\beta$ -guaiacyl Ether (**1**), and Purification and Identification of the Reaction Products

A mixture of *erythro* and *threo* forms of compound **1** was synthesized and a *threo* form was crystallized according to the method of Hosoya et al.<sup>[6]</sup> The *threo* isomer of compound **1** (19.5 mg, 0.06 mmol) was treated with 70 wt% aqueous 1,3-butanediol solution (6 mL) at 160–200°C in the presence and absence of five equivalents of glucose (54 mg, 0.3 mmol) in a stainless steel autoclave (10 mL). After heating for the prescribed time, 2 mL of the reaction mixture was withdrawn, and 100  $\mu$ L of 2-naphtol solution (500 mg in 50 mL of dioxane) was added as an internal standard. The mixture, diluted with water (20 mL), was extracted with ether (20  $\times$  2 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated carefully in vacuo at 30°C. The residue was trimethylsilylated with *bis*(trimethylsilyl) acetoamide (BSA) (0.5 mL) at 70°C for 1 h.

### Gas Chromatography (GC) and Mass Spectrometry (MS)

Silylethers of the reaction products were analyzed by GC and GC-MS. A Hitachi 263-30 Gas Chromatograph equipped with an FID was used. Trimethylsilylated reaction mixtures were injected into a TC-17 fused silica gel capillary column (GL Sciences Inc. 0.25  $\mu$ m  $\times$  30 m). The temperature program was 100–280°C at 7.5°C/min. The temperatures of the injection and detector zones were 280°C. The typical nitrogen (carrier gas) pressure was 0.8 kg/cm<sup>2</sup>; hydrogen 1.2 kg/cm<sup>2</sup>; and air 1.0 kg/cm<sup>2</sup>. Mass spectrometric analyses were performed with a JEOL JMS AX-500 using an electron energy of 70 eV.

### Gel Permeation Chromatography (GPC)

GPC analysis was performed on a HITACHI L-6200 Liquid Chromatograph with an L-4000 UV detector (280 nm) using polystyrene



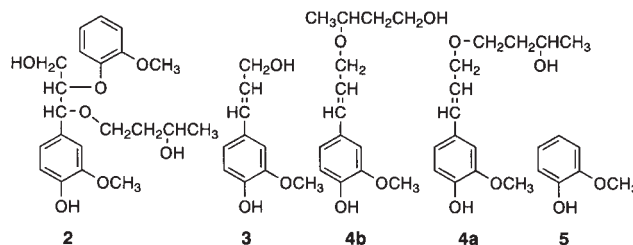
standards for calibration. A Shodex GPC KF-801 packed column (30 cm × 8.0 mm) was used with THF as the solvent (0.5 mL/min, 50°C). A reaction mixture was diluted with THF and analyzed directly without purification of the products.

## RESULTS AND DISCUSSION

### Effect of Glucose on the Degradation of a Phenolic $\beta$ -Ether Lignin Model Compound

In order to understand more about the effect of reducing sugars on delignification during HBS pulping, a phenolic  $\beta$ -O-4 type lignin model compound, guaiacylglycerol- $\beta$ -guaiacyl ether (**1**) was treated with a 70 wt% aqueous 1,3-butanediol solution in the presence of five equivalents of glucose at 180°C. The reaction products were analyzed by gas chromatography and mass spectroscopy. From reaction mixtures,  $\alpha$ -ether **2**, coniferyl alcohol (**3**),  $\gamma$ -ethers **4a**, **4b**, and guaiacol (**5**) were identified (see Fig. 3). The products were the same as those in the absence of glucose as described in the first part of this series.<sup>[2]</sup> The results in the presence and absence of glucose are summarized in Tables 1 and 2. The disappearance of starting material **1** was enhanced by the presence of glucose as shown in Fig. 4. The disappearance of compound **1** followed first-order kinetics both in the absence and presence of glucose. The rate constants were  $3.65 \times 10^{-2} \text{ min}^{-1}$  ( $r^2 = 0.992$ ), and  $6.11 \times 10^{-2} \text{ min}^{-1}$  ( $r^2 = 0.993$ ) at 180°C in the absence and presence of glucose, respectively. The rate of disappearance of compound **1** increased by a factor of 1.67 in the presence of five equivalents of glucose.

This is partly because the formation of compound **2** was also enhanced by the presence of glucose as shown in Fig. 4. Compound **2**



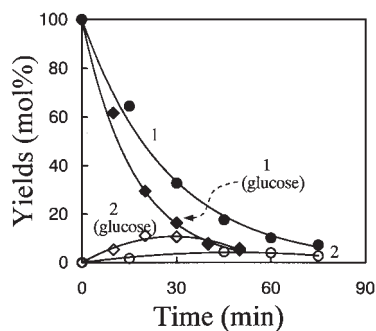
**Figure 3.** Reaction products obtained by the treatment of compound **1** in 70 wt% aq. 1,3-butanediol at 180°C.

**Table 1.** Reaction of compound **1** in the absence of glucose at 180°C.

Time (min)	Compound (mol%)				
	1	2	3	4	5
0	100	0	0	0	0
15	64.5	1.7	2.5	—	12.4
30	32.8	—	2.8	3.3	27.1
45	17.6	4.4	2.5	4.0	26
60	10.1	4.0	2.4	5.7	37.2
75	7.3	2.7	2.6	7.2	38.2

**Table 2.** Reaction of compound **1** in the presence of five equivalents of glucose at 180°C.

Time (min)	Compound (mol%)				
	1	2	3	4	5
0	100	0	0	0	0
10	61.7	5.4	4.4	9.0	10.7
20	29.5	11.1	5.0	21.7	21.0
30	16.4	10.6	6.0	30.5	31.8
40	7.5	7.9	7.2	37.7	30.6
50	5.1	5.9	7.3	39.1	44.7

**Figure 4.** Yields of compounds **1** and **2** in the presence (■, □) and absence (●, ○) of five equivalents of glucose at 180°C.



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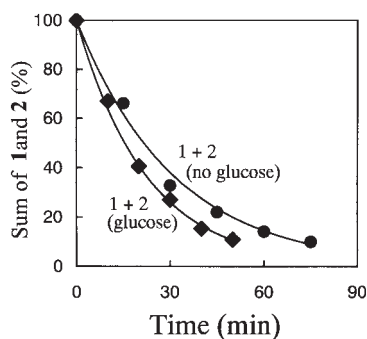
seemed to be formed by the addition of 1,3-butanediol to a quinone methide intermediate and/or the direct attack on the potential benzyl cation. It should be noted that only primary hydroxyl groups in 1,3-butanediol participated in the ether formation.<sup>[2]</sup> In the absence of glucose only 4.4% of compound **2** was formed as shown in Table 1. On the other hand, 11.1% of compound **2** was formed by the treatment of compound **1** for 20 min in the presence of glucose as shown in Table 2. The pH of the reaction mixture decreased to 3.8 and 4.1 in the presence and absence of glucose, respectively, where the pH of the mixture was measured at room temperature after the reaction mixture was diluted 10 times with water. The benzyl ether formation might have been accelerated by the lower pH in the presence of glucose at high temperature. However, the acidity was not strong enough to cause acid hydrolysis of  $\beta$ -aryl ether bond in compound **1**. No acidolysis products such as Hibbert's ketones were detected in the presence of glucose.

As described above, two main reactions were observed with compound **1** in aqueous 1,3-butanediol solutions at high temperature. One reaction is the cleavage of the  $\beta$ -aryl ether bond, and another is the benzyl ether formation with 1,3-butanediol. The benzyl ether formation is reversible, and may compete with the benzyl ether formation with glucose which is a kind of polyol. However, it was assumed that glucose did not participate in such reactions, because the concentration of glucose was much lower than that of 1,3-butanediol under the conditions used. Thus, the extent of cleavage of  $\beta$ -aryl ether was estimated by the disappearance of the sum of compounds **1** and **2** in the absence of glucose.<sup>[2]</sup>

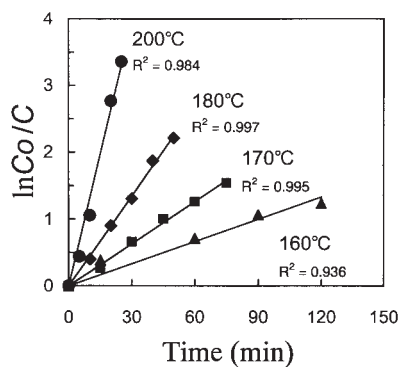
Addition of five equivalents of glucose increased the disappearance of the sum of compounds **1** and **2** at 180°C as shown in Fig. 5. The disappearance of the sum of compounds **1** and **2** followed pseudo-first-order kinetics regardless of the presence of glucose. The rate constants were  $3.22 \times 10^{-2} \text{ min}^{-1}$  ( $r^2 = 0.989$ ) and  $4.49 \times 10^{-2} \text{ min}^{-1}$  ( $r^2 = 0.997$ ) at 180°C in the absence and presence of glucose, respectively. These results suggested that the  $\beta$ -aryl ether cleavage increased in the presence of glucose at 180°C.

In order to understand the effect of glucose on the  $\beta$ -aryl ether cleavage in detail, the treatment of compound **1** was conducted at 160, 180, and 200°C in the presence of five equivalents of glucose. The rate constants for the disappearance of the sum of compounds **1** and **2** were  $1.11 \times 10^{-2} \text{ min}^{-1}$  at 160°C ( $r^2 = 0.936$ ),  $2.10 \times 10^{-2} \text{ min}^{-1}$  at 170°C ( $r^2 = 0.995$ ),  $4.49 \times 10^{-2} \text{ min}^{-1}$  at 180°C ( $r^2 = 0.997$ ), and  $13.9 \times 10^{-2} \text{ min}^{-1}$  at 200°C ( $r^2 = 0.984$ ) as shown in Fig. 6. The activation energy for the disappearance of the sum of compounds **1** and **2** was





**Figure 5.** Effect of five equivalents of glucose on the consumption of the sum of compounds **1** and **2** in 70 wt% aq. 1,3-butanediol at 180°C.



**Figure 6.** Consumption of the sum of compounds **1** and **2** in the presence of five equivalents of glucose in 70 wt% aq. 1,3-butanediol at 180°C,  $C_0$ : initial concentration of the sum of compounds **1** and **2**,  $C$ : concentration of the sum of compounds **1** and **2**.

calculated to be 98.3 kJ/mol ( $r^2 = 0.997$ ) and 108.5 kJ/mol ( $r^2 = 0.998$ ) in the absence and presence of glucose, respectively (Fig. 7). The higher value of activation energy was obtained in the presence of glucose, although the consumption of the starting material **1** was enhanced.

The results were basically in agreement with the results obtained from HBS pulping of todo fir.<sup>[4]</sup> The delignification rate of todo fir in the recovered solvent was 1.5 times greater than that with a fresh solvent. The activation energy for the delignification was 117.9 kJ/mol in the fresh solvent, and was 135.8 kJ/mol in the recovered solvent. The higher value of activation energy was obtained in the recovered solvent. It is also



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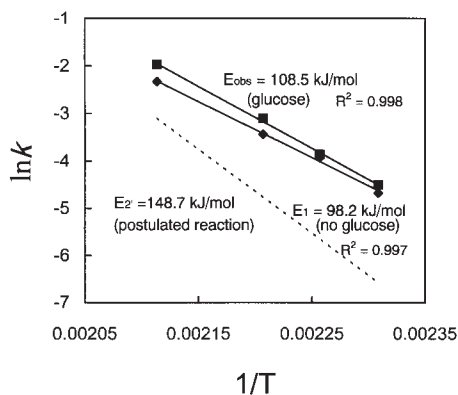


Figure 7. Arrhenius plots for the disappearance of the sum of compounds 1 and 2.

reported that addition of 10% of glucose on chips to the fresh solvent accelerated the delignification rate dramatically. The delignification rate increased in the presence of glucose by a factor of 2.0 at 220°C. However, the addition of *p*-cresol, which is a model compound for the soluble lignin in the recovered solvent, did not affect the delignification rate of todo fir. Thus, the improved effect by the recovered solvent was attributed to reducing sugars which exist in the recovered solvent.

Kinetic data obtained from the disappearance of the sum of compounds 1 and 2 suggested that in addition to homolysis of the  $\beta$ -aryl ether bond a glucose-assisted reaction might be involved in the degradation of compound 1 in the presence of glucose in aqueous 1,3-butanediol solution. If the reaction is assumed to occur as a parallel reaction to homolysis of the  $\beta$ -aryl ether, the kinetic data may be understood more properly. The activation energy of the postulated reaction must be higher than that of homolysis of the  $\beta$ -aryl ether, because the higher value of activation energy was obtained in the presence of glucose as described above. In the case under consideration, the disappearance rate of the sum of compounds 1 and 2 in the presence of glucose can be divided into two terms, which represent the rates for the homolysis of the  $\beta$ -ether ( $k_1$ ) and for the glucose assisted reaction (postulated reaction) ( $k_2$ ).

$$\begin{aligned} -d[1 + 2]/dt &= k_1[1 + 2] + k_2[1 + 2] [\text{Glucose}]^n \\ &= (k_1 + k_2 [\text{Glucose}]^n) [1 + 2] \end{aligned}$$



where  $k_1$  is first order rate constant for the disappearance of the sum of compounds **1** and **2** in the absence of glucose, and  $k_2$  is rate constant for the postulated reaction. Under the conditions used, the concentration of glucose and its degradation products are considered to be constant during the rate measurements, because a large excess amount of glucose was used in these experiments. Thus,  $k_2 [\text{Glucose}]^n$  is considered to be constant ( $k'_2$ ) and the rate expression becomes

$$\begin{aligned} -d[\mathbf{1} + \mathbf{2}]/dt &= (k_1 + k'_2) [\mathbf{1} + \mathbf{2}] \\ &= k_{\text{obs}} [\mathbf{1} + \mathbf{2}] \end{aligned}$$

where  $k'_2$  is pseudo-first order rate constant for the postulated reaction. In this case,  $(k_1 + k'_2)$  corresponds to the observed pseudo-first order rate constant ( $k_{\text{obs}}$ ) for the disappearance of the sum of compounds **1** and **2** in the presence of five equivalents of glucose. Thus, the value of  $k'_2$  can be calculated from  $k_{\text{obs}}$  and  $k_1$ . Figure 7 shows the temperature dependence of rate constants between 160 and 200°C. Dotted line indicates the calculated value of  $k'_2$ . From the Arrhenius equation, the activation energy for the postulated reaction was assumed to be 148.7 kJ/cal. Thus, the postulated reaction is considered to follow pseudo-first order kinetics with respect to the sum of compounds **1** and **2** in the presence of glucose, where the activation energy is higher than that for homolysis of  $\beta$ -O-4 bond. It is reasonably assumed from the Arrhenius equation that the postulated reaction becomes more important at higher temperature.

In connection with the postulated reaction caused by glucose, Fullerton and Wright reported that several reducing sugars and ascorbic acid substantially increased the formation of products derived from  $\beta$ -ether cleavage of phenolic  $\beta$ -aryl ether lignin model compounds under soda pulping conditions at 135–170°C.<sup>[7]</sup> The sugar-derived endiol assisted  $\beta$ -aryl ether cleavage was proposed to proceed as shown in Fig. 8.<sup>[8]</sup> They reported that reaction of the quinone methide of 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-ethanol with L-ascorbic acid gives a carbon-carbon bonded intermediate formed by the reaction of the ascorbic acid endiol with the  $\alpha$ -carbon of the quinone methide. This intermediate then fragmented under alkaline conditions to guaiacol. The reaction mechanism was similar to the well established anthraquinone mechanism. However, the efficiency of the additives decreased above 155°C, because the degradation of reducing sugars becomes a significant competing reaction under alkaline conditions at higher temperature.

Barrow et al.<sup>[9]</sup> reinvestigated the effect of glucose on the reactions of guaiacylglycerol- $\beta$ -guaiacyl ether (**1**) over a pH range of 7 to 14



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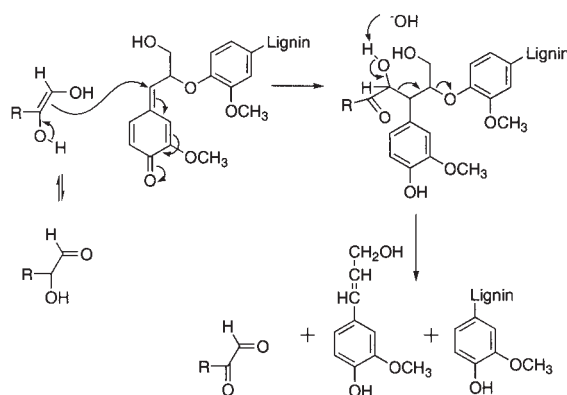
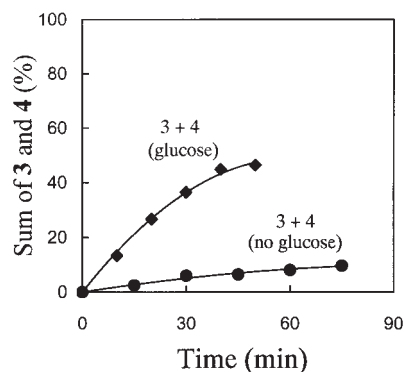


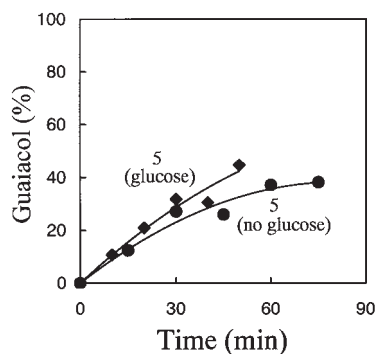
Figure 8. Endiol assisted  $\beta$ -aryl ether cleavage proposed by Fullerton and Wilkins (1985).

at 110–150°C. High yields of guaiacol (**5**) and coniferyl alcohol (**3**) were evident at lower pH and the yields were higher than those without glucose, suggesting that at low pH values glucose or its degradation products facilitate decomposition of the quinone methide. This suggests that the participation of hydroxide ion is not necessary for the glucose-assisted cleavage of  $\beta$ -aryl ethers at high temperature. Their conditions at pH 7 are comparable to the neutral or slightly acidic conditions used in this investigation. Thus, it seems reasonable to suppose that reducing sugar-assisted  $\beta$ -aryl ether cleavage might cause the additional degradation of compound **1** in the presence of glucose at elevated temperature under HBS pulping conditions.

The enhancement of  $\beta$ -aryl ether cleavage by the presence of glucose was also evident from the increase in the yields of products in our experiments as well as the results of Barrow et al.<sup>[9]</sup> Addition of five equivalents of glucose dramatically increased the yield of the sum of coniferyl alcohol (**3**) and its  $\gamma$ -ethers (**4a**, **4b**) as shown in Fig. 9. In the absence of glucose the yields of **3** and **4** were 2.6 and 7.2% at 75 min, respectively as shown in Table 1. On the other hand, 7.3% of **3** and 39.1% of **4** were formed in 50 min in the presence of five equivalents of glucose. Formation of guaiacol (**5**) was also enhanced by the presence of glucose as shown in Fig. 10. Figure 11 shows the effect of reaction temperature on the formation of guaiacol (**5**), and Fig. 12 the sum of compounds **3** and **4**. These results clearly indicate that the reaction temperature was an important factor, not only for the disappearance of starting material but for the formation of monomeric products in the



**Figure 9.** Effect of glucose on the formation of the sum of coniferyl alcohol (3) and its  $\gamma$ -ethers (4a, 4b) in 70 wt% aq. 1,3-butanediol at 180°C.



**Figure 10.** Effect of glucose on the formation of guaiacol (5) in 70 wt% aq. 1,3-butanediol at 180°C.

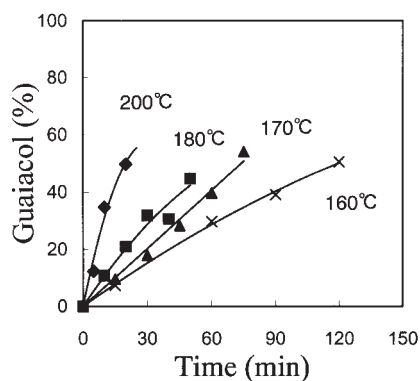
presence of glucose. A part of the increase in the yields of these products may be attributed to reactions other than homolytic cleavage of  $\beta$ -O-4 bond such as sugar-derived endiol assisted  $\beta$ -aryl ether cleavage.

However, the increase in the yields of coniferyl alcohol (3) and its  $\gamma$ -ethers (4) by the addition of glucose was much greater than that in the cleavage of  $\beta$ -aryl ether estimated from the disappearance of the sum of compounds 1 and 2. These results suggest that the phenoxy radicals formed by homolytic cleavage of the  $\beta$ -aryl ether were stabilized, and that recombination of radical species was suppressed by the reducing sugar. This is more obvious from gel permeation chromatograms of reaction products at 180°C (Fig. 13). The products with retention times

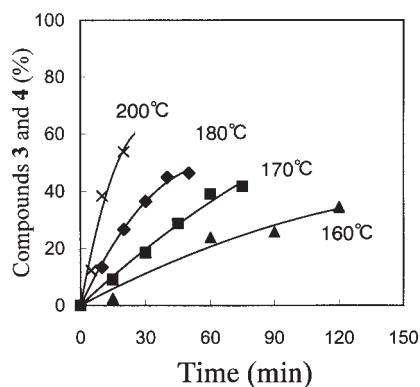


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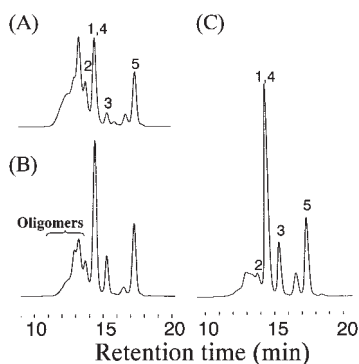
**Figure 11.** Effect of reaction temperature on the formation of guaiacol (5) in the presence of five equivalents of glucose.



**Figure 12.** Effect of reaction temperature on the formation of the sum of coniferyl alcohol (3) and its  $\gamma$ -ethers (4a, 4b) in the presence of five equivalents of glucose.

between 11.5 min and 14.0 min correspond to dimers, trimers and others formed by recombination of phenoxy radicals, which include  $\beta$ -5,  $\beta$ - $\beta$ , 4-*O*-5, 1-5 structures.<sup>[3]</sup> In the presence of five equivalents of glucose the yields of recombination products decreased dramatically as shown in Fig. 13. The presence of one equivalent of glucose was also effective at reducing radical coupling products.

Similar results are also reported in the literature.<sup>[10]</sup> Omori et al. investigated mild hydrolysis of  $\beta$ -*O*-4 lignin model compounds in the absence and presence of holocellulose. They heated compound 1 with



**Figure 13.** Effect of glucose on the formation of radical recombination products in 70 wt% aq. 1,3-butanediol at 180°C, (A) without glucose at 45 min, (B) with 1 equiv. glucose at 45 min, (C) with 5 equiv. glucose at 50 min.

dioxane/water at 180°C for 20 min, and identified 1,2-diguaiacylpropane-1,3-diol ( $\beta$ -1), dehydroconiferyl alcohol ( $\beta$ -5), DL-pinoresinol ( $\beta$ - $\beta$ ), and a trilignol in the absence of hollocellulose. These products were produced by recombination of phenoxy radicals derived from homolytic cleavage of the phenolic  $\beta$ -O-4 linkage in compound **1**. However, when this model compound was treated in the presence of hollocellulose, none of the secondary products were isolated in the reaction mixtures, except the  $\beta$ -1 compound in only a trace amount. Thus, they concluded that carbohydrates act as hydrogen atom donor, reducing the radical species before the occurrence of recombination of the radicals.

Westermarck et al. also treated compound **1** in dioxane/water (1:1) at 180°C in the presence of FeCl<sub>2</sub>.<sup>[11]</sup> They reported that addition of catalytic amount of Fe<sup>2+</sup> gave a considerably higher and also more reproducible yield of coniferyl alcohol. However, the addition of Fe<sup>2+</sup> did not affect the disappearance of the  $\beta$ -ether model compound. As suggested by Iwanade et al.,<sup>[12]</sup> these results seem to indicate that Fe<sup>2+</sup> acts as an electron donor, reducing phenoxy radicals formed by homolytic cleavage of the  $\beta$ -ether to produce coniferyl alcohol. Thus, it may be assumed that glucose as well as Fe<sup>2+</sup> stabilizes the phenoxy radicals to prevent the formation of radical coupling products. On the other hand, the addition of *p*-cresol, which is a model compound for soluble lignin in recovered solvent, did not affect the delignification rate of todo fir.<sup>[4]</sup> This is probably because *p*-cresol radicals can be generated by radical transfer mechanisms and produce radical coupling products as demonstrated by Li and Lundquist.<sup>[13]</sup> Soluble lignin in the recovered solvent may not reduce the formation of radical coupling

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products, although further investigations are necessary to elucidate the role of soluble lignin in more detail.

**CONCLUSIONS**

In order to understand more about the role of reducing sugars present in the recovered solvent during HBS pulping, a phenolic lignin model compound with  $\beta$ -O-4 bond was treated with 70% aqueous 1,3-butanediol solutions. Addition of glucose increased the consumption of the starting material and decreased the radical coupling compounds dramatically. These results suggest that reducing sugars may play an important role during solvent pulping under neutral or slightly acidic conditions, although further investigations are necessary to elucidate the reaction mechanisms more clearly and also to evaluate the extent of such reactions during pulping.

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