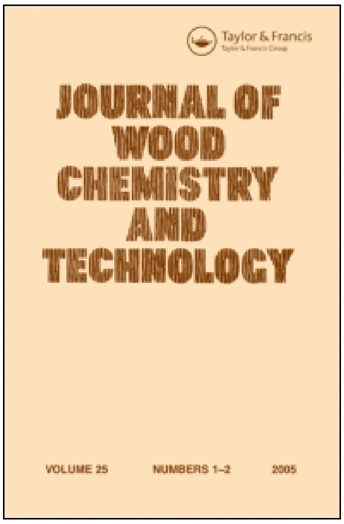

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FORMATION OF ISOEUGENOL AND EUGENOL DURING THE CLEAVAGE OF β-ARYL ETHERS IN LIGNIN BY ALCOHOL-BISULFITE TREATMENT[1]

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ABSTRACT

Treatment of guaiacylglycerol- and guaiacylpropanediol-β-(2-methoxyphenyl) ethers at 160 C in 50 % alcohol containing magnesium bisulfite was found to cleave the β-aryl ether linkages in these compounds to form isoeugenol and/or eugenol in up to 60 % yield as well as comparable yields of guaiacol. The linkage in a nonphenolic model was not cleaved to a discernible extent. Both an alcohol and bisulfite were essential for this reductive cleavage which proceeded efficiently in ethanol and isopropanol but not efficiently in methanol, t-butanol or dioxane. Magnesium was a better base than sodium for the reaction.

Coniferyl alcohol was proposed to be an intermediate compound of this cleavage reaction which reasonably explains the formation of isoeugenol and eugenol from wood during the alcohol bisulfite pulping process.

INTODUCTION

Solvent sulfite pulping which contains alcohol and bisulfite ion in a cooking liquor has been recently proposed as an effective organosolv pulping method. This method gave stronger pulps than ordinary bisulfite pulps at the same yield and higher yields than kraft pulps at the same Kappa number levels, and it can be successfully applied to different wood species[2-5]. Concerning the mechanism of delignification during this pulping process, it is believed that the accelerlated delignification observed when an alcohol is present might be due to sulfonation of the lignin and increased solubility or accessibility of the lignin in alcohol.

Recently we found that isoeugenol (**6**) and eugenol (**7**) were formed as major products of the alcohol bisulfite pulping of a softwood[6]. A combined yield of these products was about 4.5 % on lignin in original wood. This high value for a yield of lignin-derived phenyl propanoids suggested that the origin of these products is the β-O-4 type dilignol substructure. Furthermore, production of **6** and **7** is very characteristic of this pulping process since we have not seen any literature which reported isolation of such a high yield of these compounds from lignin degradation, though much lower yield of **6** and **7** was reported in sodium bisulfite cooking of Pinus radiata[7,8].

Treatment of lignin model compounds having the β-O-4 type substructure under conditions similar to those used for alcohol sulfite pulping also gave products **6** and **7**. The present paper deals with the characteristics of this cleavage reaction which so far has not been reported in literature. The optimum reaction condition for this cleavage has also been studied briefly.

EXPERIMENTAL

1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (**1**)[9], 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1-propanol (**2**)[10], and 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1-propanol (**3**)[11] were prepared by the known methods.

Model Compound Treatment and Product Determination

A model compound (0.1 m mol) and 50 % alcohol solution (1.5 mL, pH 4.5) containing 0.23 m mol of magnesium bisulfite were mixed in a glass ampoule (5 mL in volume). The ampoule sealed on a flame was heated in a glycol bath at 160°C and then cooled rapidly in running water after a prescribed period of reaction time. Contents in the ampoule (pH 2.5-3) were mixed with an aqueous alkali containing 4-hydroxy-3-methoxytoluene (50 u mol) as an internal standard. The mixture was acidified with diluted hydrochloric acid, extracted with ether and the ether extract analyzed for guaiacol, eugenol and isoeugenol by means of GLC and GC-MS. Column: 5 % SE30 (3 mm x 2 m), temp.: 100-160°C (programmed at 5 C/min), ionization potential: 70 eV, and retention times of guaiacol, eugenol, and E- and Z-isoeugenol were 5.5, 11.4, 12.7 and 13.7 min, respectively.

The aqueous phase obtained after the ether extraction was diluted 10 times either with water or with 0.1 N NaOH prior to UV spectrum measurement. Yield of water soluble product(s) was estimated as α-sulfonic acid of starting material based on absorbance at 277 nm because acidic and alkaline spectra of the aqueous solution were similar to those of the starting compounds **1** and **2** (λ_{max} 277 nm in H_2O, 280 and 293 nm in 0.1 N NaOH).

Determination of Coniferyl Alcohol in Wood Meal Cooking

Sugi (*Cryptomeria japonica* D. Don) wood meal (2.5 g) extracted with ethanol-benzene was mixed with 50 % isopropanol (15 mL) containing magnesium bisulfite (6.3 % as SO_2 on wood), sealed in a stainless steel autoclave with a screw cap, and heated in a glycol bath. The temperature of the bath was elevated to 165 C in 90 min and then kept constant. At a prescribed time, the autoclave was cooled in water. One mL aliquots of spent liquor recovered by filtration of the pulping mixture were used for determination of coniferyl alcohol by means of HPLC. Column: Novapack C18 (3.9 mm x 15 cm), solvent: 8/92 CH_3CN/0.01 M phosphate buffer (pH 3) at a flow rate 0.8 mL/min, and retention time of coniferyl alcohol: 25.6 min. If a solvent ratio 15/85 was used coniferyl alcohol and dihydroconiferyl alcohol appeared at an identical retention time 7.05 min.

RESULTS AND DISCUSSION

Characteristics of the Reaction

Guaiacylglycerol-β-(2-methoxyphenyl) ether **1** and guaiacylpropanediol-β-(2-methoxyphenyl) ether **2** chosen as phenolic β-O-4 type models were treated at 160°C with a 50 % isopropanol solution containing magnesium bisulfite. These are the reaction condition normally used for pulping by us[3,5]. E-isoeugenol **6** and eugenol **7** in addition to guaiacol **4** were obtained from compound **1** in about 40 % yield by the treatment for 50 min as shown in Table 1. (See Scheme 1 for the structure of each compound.) The compound **2** gave **6** in a yield about 40 %, though **7** was not produced. These data indicated that the β-aryl ether linkages in phenolic models are extensively cleaved with formation of **6** and **7** under the alcohol sulfite pulping condition.

In order to know if both the alcohol and bisulfite are essential for the cleavage of the β-aryl ether linkages during the alcohol sulfite delignification, compound **1** and **2** were treated either with a bisulfite solution in pure water or with an acidic alcohol-water mixture (pH 4.5) which contained no bisulfite ion. As seen from the yield of guaiacol **4** in Table 1, a substantial part of the β-aryl ether bonds in **1** and **2** were cleaved in 50 % isopropanol solution which had been adjusted to pH 4.5 with hydrochloric acid prior to the treatment. This cleavage reaction is supposed to have proceeded through so called alcoholysis mechanism. However, it was much slower than in the alcohol sulfite solution at the same pH and gave neither **6** nor **7**.

TABLE 1

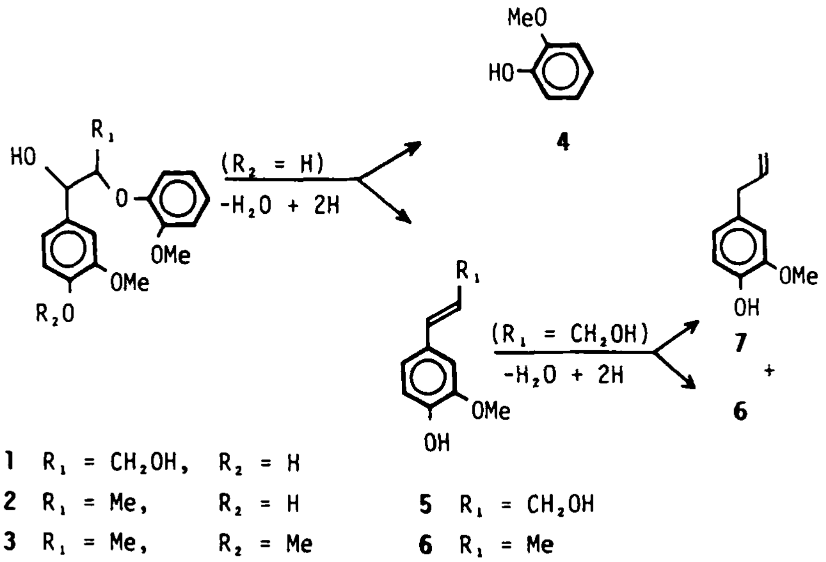
Cleavage of β-O-4 Linkages in Compounds **1** and **2**
by the Solvent-sulfite Treatment at 160°C

Model[*1] Compounds	MB,[*2] % as SO_2	IPA[*3] %	Time min.	Product[*1] yield, mol %				
				4	**6**	**7**	**6+7**	S
1	2.0	50	50	53	28	14	42	27
	2.0	50	120	64	26	15	40	35
	2.0	0	50	15	0	0	0	58
	2.0	0	120	10	0	0	0	22
	0.0	50	50	26	0	0	0	0
	0.0	50	120	43	0	0	0	0
2	2.0	50	50	43	41	0	41	20
	2.0	50	120	53	39	0	39	34
	2.0	0	50	12	0	0	0	44
	2.0	0	120	15	0	0	0	36
	0.0	50[*5]	50	18	0	0	0	0
	0.0	50[*5]	120	33	0	0	0	0
5	2.0	50	60	0	24	12	36	--

*1 See scheme 1 for the structure of each compound.
*2 MB = Magnesium bisulfite. *3 IPA = Isopropanol.
*4 S = Water-soluble products, calculated as an alpha-sulfonate based on UV absoption. *5 Acidified by HCl to pH 4.5.

An aqueous sulfite solution without any alcohol caused slower cleavage of the β-aryl ether linkages presumably via the sulfitolysis mechanism found by Gellerstedt *et al.*[12] to occur during the neutral sulfite treatment for a longer time (3h) at a higher temperature (180°C). This view might be supported by the presence of water soluble products, probably sulfonates, which had UV spectra similar to those of the starting materials. However, neither **6** nor **7** were detected in this case, either.

The results described above indicate that the arylglycerol-β-aryl ether linkages in lignin are extensively cleaved under the



Scheme 1

condition of the alcohol bisulfite pulping and produce isoeugenol (**6**) and eugenol (**7**) as lignin-derived products. This reaction has not been reported to date, being completely different from alcoholysis or sulfitolysis known to occur under conditions similar to that of the alcohol sulfite pulping.

Influence of Reaction Condition

The β-ether model compound **2** was employed to investigate influence of reaction conditions on the cleavage mentioned above since rate of the cleavage of this compound was similar to that of guaiacylglycerol-β-(2-methoxyphenyl) ether (**1**) and the product composition from this compound was simpler than that from the compound **1** as shown in Table 1. Influence of different solvents i.e. methanol, ethanol, isopropanol, t-butanol and dioxane is

TABLE 2

Influence of Solvents and Bases on the Yield of Guaiacol (**4**) and Isoeugenol (**6**) Formed From Compound **2** During Solvent Sulfite Treatment.*1

Solvent	Base	Product*2 yield, mol % **4**	**6**
MeOH	Mg	26	13
EtOH	Mg	59	59
EtOH	Na	59	36
i-PrOH	Mg	45	44
i-PrOH	Na	38	29
t-BuOH	Mg	25	5
Dioxane	Mg	14	10

*1 Solvent concn.: 50 %, Bisulfite concn.: 2 % as SO_2, at 160°C for 50 min.

*2 See scheme 1 for the structure of each compound.

shown in Table 2. Ethanol gave the better yield (ca. 60 %) of **6** than isopropanol which we have used for cooking of wood. Methanol, t-butanol and dioxane gave much worse results, although the reason why the different solvents gave different yields of the products is not understood yet. Table 2 also suggested that magnesium is a more suitable base of bisulfite than sodium for the reductive cleavage reaction.

Concerning alcohol concentration, the best yield of **6** was obtained in 50 % ethanol as indicated in Fig. 1. The same Fig. also demonstrated that a different type of cleavage, probably hydrolysis[13,14], of the compound **2** proceeded quite extensively without formation of isoeugenol at the higher alcohol concentration. However, the β-ether linkages in wood lignin are not likely to suffer from hydrolytic cleavage so extensively as in compound **2** at the high alcohol concentration, since Hoo and Sarkanen[14] found that the hydrolytic cleavage of the compound **1** in aqueous

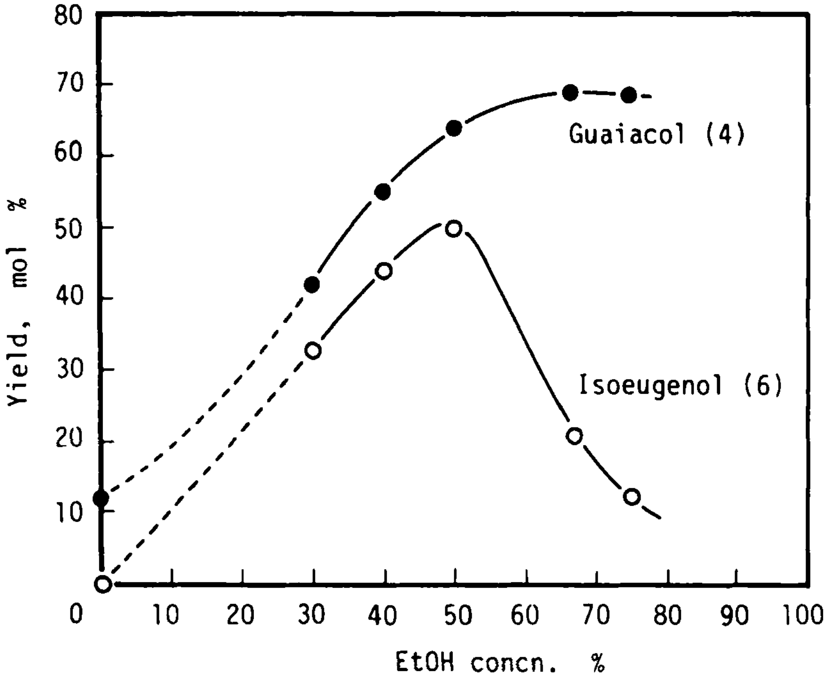


FIGURE 1. Effect of alcohol concentration on the yield of guaiacol (**4**) and isoeugenol (**6**) from the compound **2**.

dioxane and ethanol systems was depressed by the elimination of a hydroxymethyl group in the γ-position and the consequential formation of C_6C_2-enol ethers which was increased with increasing concentration of the organic solvent.

The influence of reaction conditions on the formation of **6** and **7** described above were very similar to the effects of cooking variables during the solvent sulfite pulping of wood meal[15].

A possible yield of these products from wood is calculated to be 1.5 % from the following equation:

$$Yw = Ym \times A \times B \times C$$

here, Yw: calculated yield (% of wood lignin) of isoeugenol and eugenol from softwood, Ym: their yield from model compounds (up to 60 %), A: frequency of uncondensed unit in softwood MWL (at most 50 %)[16], B: β-aryl ether linkages in softwood MWL (at most 50 %)[16], and C: phenolic hydroxyl in wood lignin (ca. 10 %)[17].

However, the yields actually obtained were 5 to 6 %[15], which is several times larger than the calculated value mentioned above. We, therefore, believe that many of nonphenolic β-O-4 substructure became phenolic during the alcohol bisulfite cooking of wood so as to produce isoeugenol and eugenol. In this connection it is worth to note that Yang et al.[18] has reported increasing phenolic hydroxyl group content during the early stage of neutral sulfite pulping.

Coniferyl Alcohol as an Intermediate Compound

When the compound **2** was cleaved by the alcohol sulfite treatment solely isoeugenol (**6**) but no eugenol (**7**) was produced as a GLC-detectable phenylpropanoid product as shown in Table 1 and 2. The product **6** can be taken as formed by a reductive cleavage of compound **2** formally through a two-electron transfer. A corresponding reaction would produce coniferyl alcohol (**5**) from compound **1**. This view strongly suggested, as illustrated in Scheme 1, that coniferyl alcohol (**5**) is an intermediate compound in the reaction of **1** yielding both **6** and **7** as well as guaiacol (**4**) as final products.

Therefore, **5** was treated with isopropanol bisulfite solution (Table 1). A combined yield of **6** and **7** was 36 % which is high enough to demonstrate that **5** could be a main intermediate compound if one takes into account the extreme sensitivity of **5** towards acids.

A further evidence to support **5** to be an intermediate was obtained by detection of this compound during the temperature-rising period of wood meal cooking. As shown in Fig. 2, the amount of **5** formed in the cooking liquor was increased until a

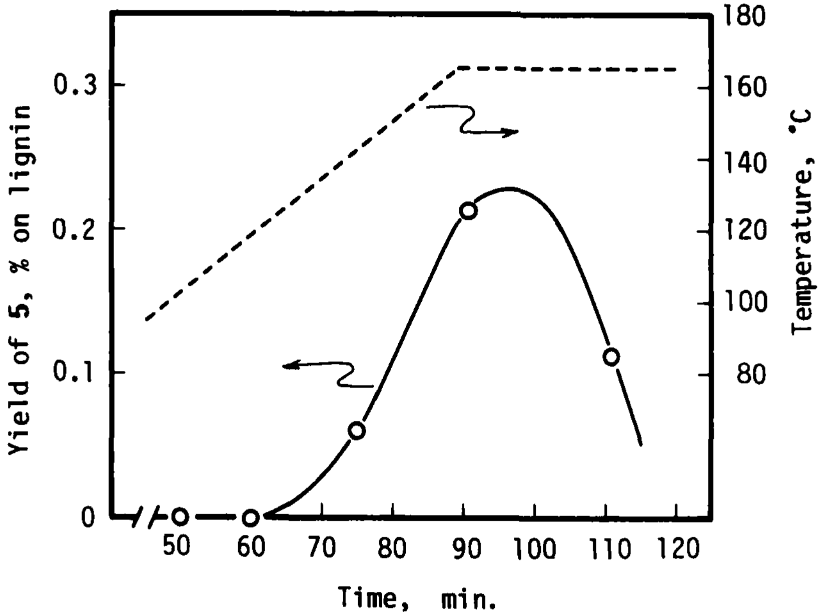


FIGURE 2. Yield of coniferyl alcohol (5) formed during the isopropanol bisulfite cooking of sugi (Japanese cedar) wood meal. Note: Time includes a temperature-rising period.

bath temperature reached 160 C then decreased rapidly at this temperature. These facts imply coniferyl alcohol 5 is a main intermediate compound in the course from the phenolic β-O-4 substructure to the monomeric lignin degradation products 6 and 7 during the alcohol sulfite pulping process.

Mortimer has recently demonstrated an initial formation of 5 and its subsequent reduction to 6 during the soda-AQ or kraft treatment of softwoods though the yield of 6 was quite low as compared with the present experiments[20]. Anthrahydroquinone or sulfide is known to act as a reducing agent during the formation of 5 in soda-AQ or kraft system. Probably bisulfite anion has such a reducing force in alcohol-water mixtures during the alcohol-bisulfite treatment. He also found that **5** was readily formed on treating lignin sulfonates with soda-AQ. However, alcohol-bisulfite treatment of a larch lignin sulfonate produced neither **6** nor **7**.

The reaction that yields **5** is likely to involve quinonemethide formation from 4-hydroxybenzyl alcohol structures because the same treatment of an etherified model compound **3** yielded no methyl ethers of isoeugenol and eugenol besides only a trace amount of guaiacol (**4**). It is interesting to note in this regards that Beatson _et al._[19] deduced recently the formation of quinonemethides from phenolic lignin units under the condition of bisulfite cooking at 120 to 150°C. The mechanism of reductive cleavage of the quinonemethides accompanied with formation of **4** and **5** and its further reduction to **6** and **7** is now being studied.

CONCLUSION

The β-aryl ether linkages were found to be cleaved by the treatment with aqueous alcohol containing bisulfite. This reaction explains well the formation of isoeugenol and eugenol from wood during the alcohol bisulfite pulping process since influence of reaction conditions on the combined yield of these products in the present model experiment was essentially the same as the effect of cooking variables such as different solvents, solvent concentration and bisulfite dose in the alcohol bisulfite delignification of wood.

Coniferyl alcohol was proposed to be a primary intermediate product presumably formed via the quinonemethide intermediates in the course of the reaction. The detailed mechanism of the reductive cleavage of the β-aryl ether linkages to yield this alcohol and further reduction of this alcohol to isoeugenol and eugenol must await further studies.

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