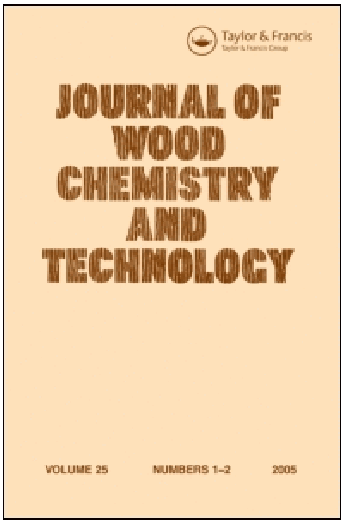

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MONOMERIC PRODUCTS FORMED FROM THE LIGNIN OF SUGI WOOD DURING ALCOHOL SULFITE PULPING[1]

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ABSTRACT

Isopropanol bisulfite treatment of sugi (Cryptomeria japonica D. Don) MWL yielded a significant amount of lipophilic low-molecular-weight products as well as water-soluble high-molecular-weight lignin whereas with an aqueous bisulfite treatment a very small amount of lipophilic products was formed and about half of the MWL was changed to insoluble and probably condensed products.

Seven monomeric and one dimeric lignin degradation products as well as two carbohydrate-derived products were found in the spent liquor from isopropanol bisulfite pulping of sugi wood of which eugenol and isoeugenol were the major products. After cooking for 50-100 minutes at 165°C, the combined yield of these two products reached a maximum of 4.5 % based on lignin, which is ten times as high as the yield of a phenolic fraction previously obtained from aqueous bisulfite pulping of Pinus radiata. Formation of the other products such as stilbene and coniferaldehyde increased gradually after 100 minutes and the combined yield was less than 0.5 %. The high yield of eugenol and isoeugenol as byproducts may increase the viability of the alcohol sulfite pulping process.

INTRODUCTION

There have been significant advances in alcohol-sulfite pulping during the last several years. We have shown that the sulfite delignification of sugi (Japanese cedar: Cryptomeria japonica D. Don) in the pH range 4 to 12 is generally accelerated

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by the presence of 50 % isopropanol in the cooking liquor[2] and that isopropanol-magnesium bisulfite can be successfully applied to different wood species among temperate soft- and hardwoods as well as tropical hardwoods[3]. Bublitz et al. examined the methanol-sulfite pulping system and showed that it was effective on hemlock, Douglas fir and mixed hardwoods; full chemical pulps being obtained in yields between 60 to 65 % in relatively short cooking times[4]. However, to our knowledge, there has been no report on the characteristics of lignin dissolved during solvent-sulfite pulping except our brief observation[5] that the dissolved lignins were of much higher molecular weight than those dissolved by the ordinary aqueous bisulfite pulping.

In the present study we have found that about 6 % of extracted sugi wood was converted into chloroform-extractable products by the isopropanol-bisulfite cooking. Nelson et al.[6-8] has previously isolated some non-sulfonated lignin fragments from a relief gas and a spent liquor of aqueous bisulfite pulping of Pinus radiata. However, the yield of an ether soluble fraction (ca. 0.5 % of wood)[9] from the aqueous bisulfite spent liquor is less than one tenth of the present result. This big difference in the yields of the lipophilic fractions suggests a different origin of those products between the aqueous and alcohol sulfite pulping. In addition, much higher yield of phenols in the present work may increase the viability of the alcohol-sulfite pulping process since some of these products are easily isolatable from the spent liquor and utilizable as perfume, flavor or medicinal raw materials.

RESULTS AND DISCUSSION

Treatment of MWL with Bisulfite

Milled wood lignin (MWL) prepared from sugi wood was treated with sodium bisulfite either in aqueous solution or in 50 % isopropanol solution at 165°C for 90 min. All the MWL employed went into solution after the isopropanol bisulfite treatment whereas about half was insoluble after the aqueous bisulfite treatment. This insoluble residue might have suffered from extensive condensation or polymerization during the aqueous bisulfite treatment because this residue was not soluble even in 90 % dioxane or 0.1 M sodium hydroxide which are known to be good lignin solvents.

Gel filtration of the spent liquor from the isopropanol bisulfite treatment (Fig. 1) revealed the formation of a long-elution-time fraction which was extractable with chloroform and corresponded to the lipophilic low-molecular-weight fraction obtained from isopropanol magnesium bisulfite cooking of different wood species described in a previous paper[3]. This fraction obviously is characteristic of the isopropanol bisulfite treatment since no such fraction could be detected on a gel chromatogram of the dissolved lignin obtained by the aqueous bisulfite treatment (Fig. 1). Therefore, we tried to identify and estimate individual compounds in this fraction as described below.

In addition to the chloroform-extractable fraction mentioned above, the isopropanol bisulfite treatment also yielded a large amount of lignosulfonate with molecular weight higher than that of the dissolved fraction of the aqueous bisulfite treated lignin as shown in Fig. 1. This suggests that a large part of the lignin suffered from some fragmentation and/or condensation, if any, to a lesser extent during the isopropanol bisulfite treatment than in the aqueous bisulfite treatment since no insoluble fraction was formed by this treatment as mentioned above. More precise knowledge of this delignification process must await further study.

Product Identification

In order to isolate the low-molecular-weight fraction mentioned above, extracted sugi wood meal was cooked in 50 % iso-

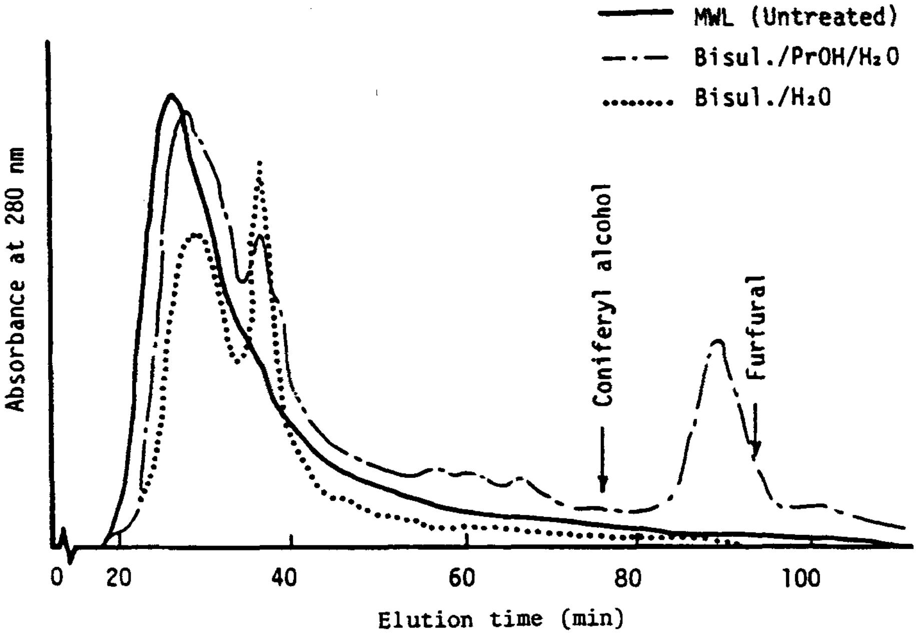

FIGURE 1. Gel chromatography of MWL untreated (——), treated with isopropanol-bisulfite (–·–), and aqueous bisulfite (·····).

propanol solution containing magnesium bisulfite (SO_2: 6.3 % based on wood) at 165 °C for 160 min. A chloroform extract (about 6 % of wood) obtained from spent liquor of this cook was purified to identify individual compounds by means of different chromatographic and spectrometric methods as described in the experimental section.

E-isoeugenol (**1**) and eugenol (**2**) were prominent products in the chloroform extracts. The other products identified were Z-isoeugenol, 4-propenylphenol (p-anol) (**3**), 4-allylphenol (chavicol) (**4**), dihydroconiferyl alcohol (**5**), 4,4'-dihydroxy-3,3'-dimethoxystilbene (**6**), coniferaldehyde (**7**), vanillin (**8**), furfural (**9**), and 5-(hydroxymethyl)-2-furfural (**10**) as shown in Fig. 2. All of these products except **9** and **10** should originate

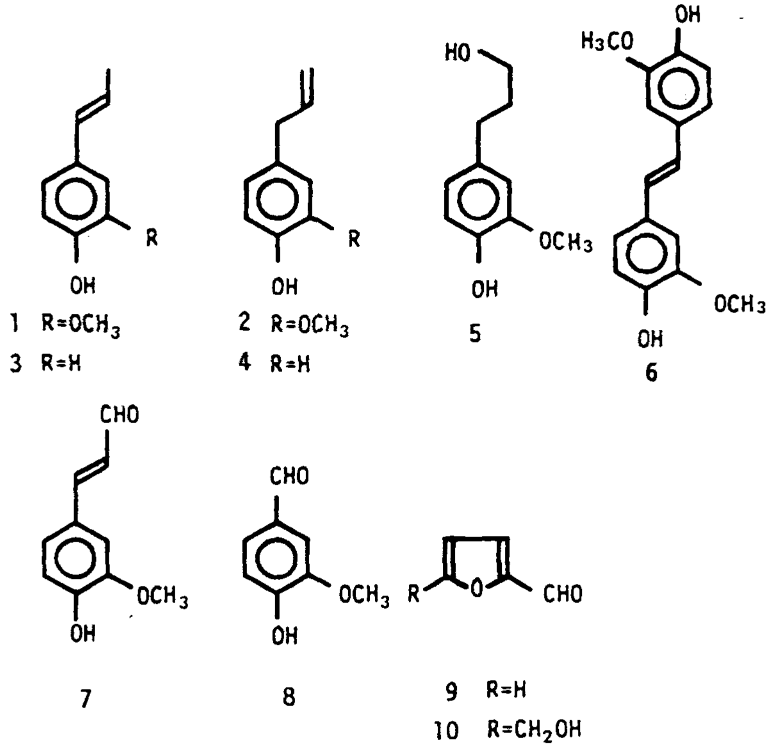

FIGURE 2. Identified products.

from lignin. The compounds 1 and 2 as well as 3, 4 and 5 are in a more reduced state than lignin precursors, coniferyl and p-coumaryl alcohol. Eugenol (2) is a major component of clove oil and is utilized as a perfume and as a flavor additive. Isoeugenol (1) is also an important intermediate in medicinal synthesis. It is interesting to note that dihydroconiferyl alcohol (5) has been reported to stimulate growth of soybean callus[10]. Compounds 6, 7 and 8 have often been detected as products of sulfite pulping[7,8] and other lignin degradation.[11]

Of these products, **1** , **2** , **6** , **8** , and **9** were previously found in a relief gas or a spent liquor from aqueous sodium bisulfite pulping of P. radiata[6-8]. However, yields of these products in the present result are markedly higher than those from the aqueous bisulfite pulping as described below.

Yield of The Low-Molecular-Weight Products

The yield of major products, E-isoeugenol (**1**) and eugenol (**2**), was compared between aqueous and alcohol bisulfite pulping. Aqueous sodium bisulfite pulping of both P. radiata and sugi produced very little **2** and trace amounts of **1**, whereas the isopropanol bisulfite pulping of the pine gave a much higher yield of **1** and **2** (1.2 % of wood) as shown in Fig. 3. The phenols formed during the aqueous bisulfite pulping is likely to originate from rather special but not common lignin substructures because yield of **2** from sugi (0.015 % of wood) was quite lower than from P. radiata (0.05 %) which seems a reasonable figure as compared with the yield of a phenolic fraction (0.15 %)[9] from a bisulfite spent liquor of the same pine species.

Yields of the products identified from sugi wood are shown on the lignin basis in Fig. 4 as a function of cooking time. A maximum total yield of the products **1** and **2** was about 4.5 % which is about the same as the yield from P. radiata, quite large for lignin degradation products, and larger by one order of magnitude than those of the other compounds in the chloroform extract. This fact suggests that these two prominent products were formed by cleavage of the β-O-4 bond which is the most frequent substructural unit in lignin. This will be shown elsewhere[12].

Yields of stilbene **6** and coniferaldehyde **7** increased gradually after 100 minutes of cooking at 165°C while the reduced compounds **1** and **2** were formed quite rapidly and reached a maximum in their yield at around 50-100 minutes. These curves may be

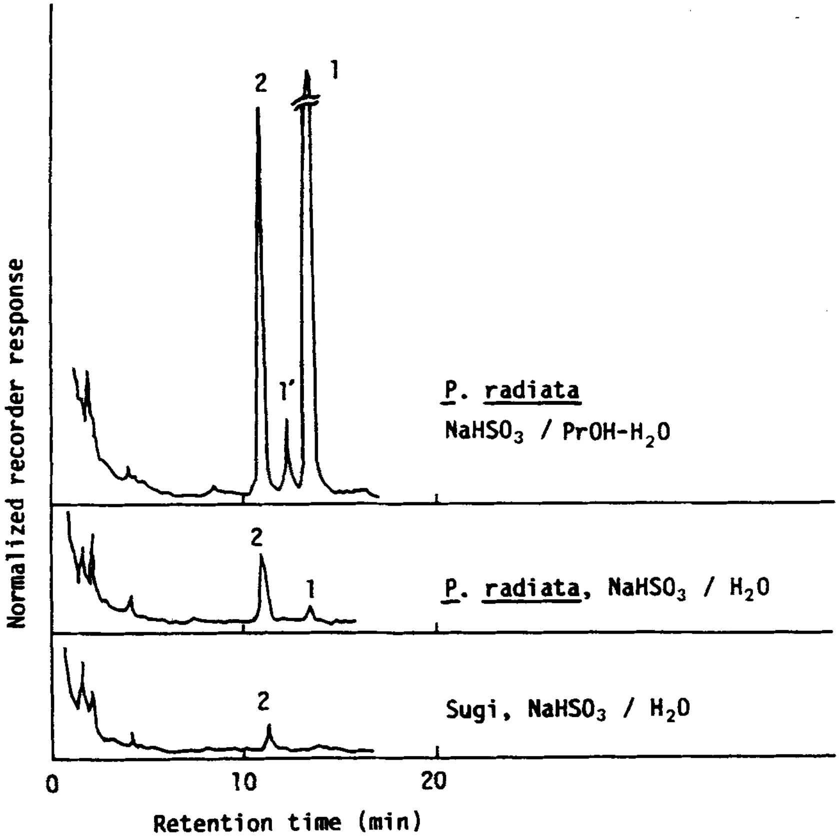

FIGURE 3. Typical gas chromatogram of chloroform extracts from spent liquors of different bisulfite cooking. 1: E-isoeugenol, 1': Z-isoeugenol, and 2: eugenol.

explained by an assumption that phenolic ethers in the lignin substructures which would yield 6 and 7 were cleaved after the peeling-like removal of the β-O-4 bonds. Another possible explanation is that an acid catalyzed hydrolysis or solvolysis yielded 6 and 7 as well as carbohydrate-derived products 9 and 10, with their formation being accelerated by the increased acidity of the cooking liquor as the cooking proceeded.

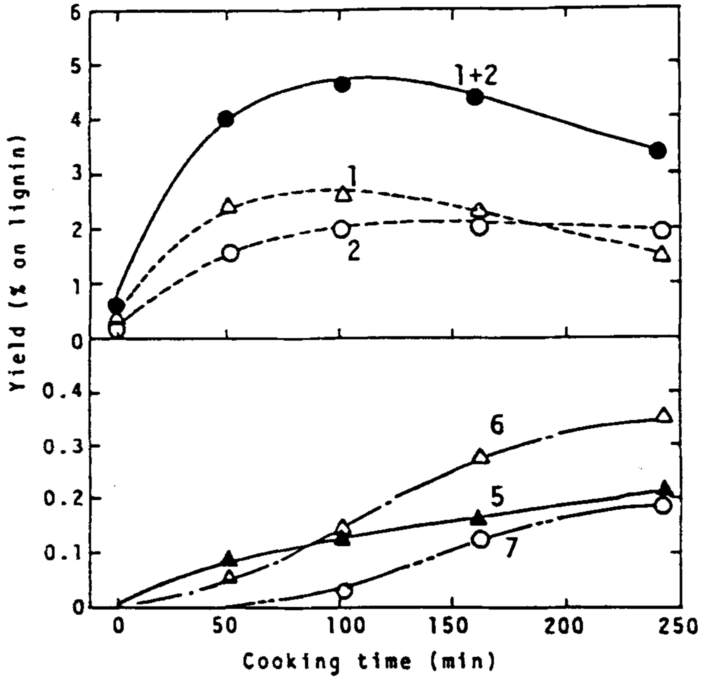

FIGURE 4. Yield of phenolic products from sugi wood as a function of time of isopropanol-bisulfite cooking.

EXPERIMENTAL

Authentic Compounds

Chavicol (4) and p-anol (3) were prepared from estragole and anethole, respectively, by the action of ethyl magnesium iodide[11]. Dihydroconiferyl alcohol (5) was prepared by the hydrogenation of coniferyl alcohol using 5 % Pd-C as a catalyst. Other compounds were commercially purchased and, if necessary, purified by distillation, recrystallization and/or preparative TLC.

Treatment of MWL and Gel Filtration

Sugi (Japanese cedar: Cryptomeria japonica D.Don) milled wood lignin (25 mg) and 2.5 mL of 0.164 M sodium bisulfite in water or in 50 % isopropanol were sealed in glass ampoules. The ampoules were placed in a stainless steel tube and heated in glycol bath to 165°C in 90 minutes. After 90 minutes at this temperature the ampoules were removed from the tube and cooled rapidly by running water. Insoluble lignin after this treatment was separated by filtration. The filtrate was diluted with 0.05 M sodium hydroxide solution and charged on a column of Toyopearl HW50F (1 x 33.5 cm) suspended in 0.05 M sodium hydroxide and then eluted by the same solvent at a flow rate 23 mL h^{-1}. Lignin in the effluents was monitored with a UV-1 detector (Pharmacia) at 280 nm.

Cooking of Wood Meal and Isolation of Lipophilic Products

Sugi wood meal (300 g) in 1.8 L of 50 % isopropanol containing 0.3 mol of $Mg(HSO_3)_2$ was heated to 165°C in 90 min and for 160 min at this temperature. The yield of cooked wood meal was 55 % and the lignin content was 6.7 % based on the original wood. A part of spent liquor (one L) recovered by filtration was extracted three times with one L of chloroform. The mixture was centrifuged (3000 rpm x 10 min) to accelerate separation of the aqueous and chloroform layers. A residue (about 10 g) after evaporation of the chloroform extract was fractionated into 10 fractions by silica gel (Wakogel C-200, 800 g) column chromatography using MeOH/$CHCl_3$ mixtures as eluents. Methanol concentration in this mixture was increased gradually from nil to 10 %.

Identification of Individual Compounds

Isoeugenol (1) and eugenol (2) were sole components of fraction 3 (oil, 1.93 g) which showed one spot on TLC (Rf=0.33 on silica gel HF254, solvent $CHCl_3$) and which by GC showed two large and one small peak with retention times which were identical with those of eugenol and E- and Z-isoeugenol, respectively. Areas of these peaks and IR spectrum of the fraction revealed that ratio of isoeugenol to eugenol was about 1 to 1. Anal. (as 2,4-dinitrophenyl ether), Cald. for $C_{16}H_{14}O_6N_2$: C 58.18, H 4.27, N 8.48 %, Found: C 58.03, H 4.23, N 8.50 %.

Fraction 4 (oil, 0.29 g) was identified as furfural (9) using TLC, GLC and HPLC.

4,4'-Dihydroxy-3,3'-dimethoxystilbene (6) (0.08 g) was crystallized from fraction 5 as colorless needles (MeOH), m. 217-217.5 °C (lit.[15] 214-216 °C). UV data was the same as in ref. 14. Anal. Cald. for $C_{16}H_{16}O_4$: C 70.57, H 5.92 %, Found: C 69.99, H 5.89 %. Diacetate m. 230-231 °C (lit.[9] 230 °C). Anal. cald. for $C_{20}H_{20}O_6$: C 67.40, H 5.66 %, Found C 67.19, H 5.75 %.

Rest of the fraction 5 after acetylation with an acetic anhydride-pyridine mixture was re-chromatographed on silica gel to afford eight fractions, F5-1 to F5-8. Only peaks of p-anol (3) and chavicol (4) were found as their acetates on GC and also HPLC of F5-1. The ratio of p-anol to chavicol in this fraction was estimated to be 3:7 from GC peak areas and NMR spectrum of this mixture. One oily fraction obtained by preparative TLC of F5-7 and F5-8 was revealed to contain two main components, 5-(hydroxymethyl)-2-furfural (10) and dihydroconiferylalcohol (5) by means of GC-MS. Besides these, vanillin (8) and coniferaldehyde (7) were detected as their acetates on GC of F5-3 and F5-4, respectively, and also on HPLC of their de-acetylated fractions.

Quantitative Determination of Product Yield

A chloroform extract of a spent liquor obtained by a small scale cooking of extracted wood meal (2.5 g) for a prescribed periods of time was evaporated to a small volume. This extract was subjected to HPLC analysis after addtion of either 4-methylguaiacol or nitrobenzene as an internal standard. The yield of each product was calculated from peak area on the basis of calibration curve which had been made for each compound. HPLC column: Nova Pack C18 (3.9 mm x 15 cm), solvent: 30/70 or 8/92 acetonitrile/0.01 M phosphate buffer (pH 3) at flow rate 0.8 mL min^{-1}

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