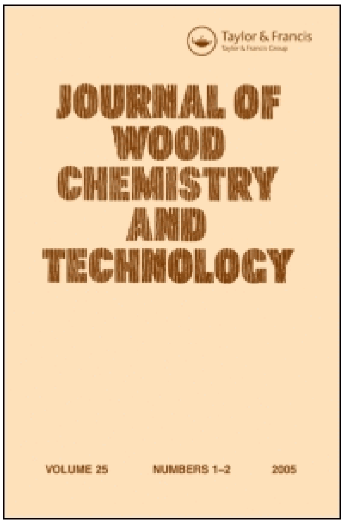

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STABILITY OF α-ETHER TYPE MODEL COMPOUNDS DURING CHEMICAL PULPING PROCESSES

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ABSTRACT

In order to examine the stability of lignin-carbohydrate complexes (LCC) during alkaline chemical pulping, benzyl ether type LCC model compounds containing different non-phenolic units were synthesized and cooked under chemical pulping conditions. At least 80% of the starting substance was recovered unchanged, from soda, kraft and acid sulfite reactions indicating the benzyl ether linkage in this compound is stable during pulping. Furthermore, by blocking the reactive benzylic hydroxyl group, the cleavage of adjacent β-ether linkages in lignin moiety is retarded.

Thus it is concluded that non-phenolic α-ether linkages between lignin and carbohydrates are stable under alkaline pulping conditions and may be the cause for the residual lignin to resist a complete delignification.

INTRODUCTION

A significant drawback of the kraft pulping process is the relatively high content of residual lignin in this pulp. To obtain a lignin free pulp, kraft pulp has to undergo a tedious multiple stage bleaching process, which is not only expensive but also prone to water pollution.

In our earlier work[1], for the purpose of improving these current pulping and bleaching processes, the residual lignin in kraft pulp was isolated by selectively hydrolyzing and dissolving the carbohydrates with cellulolytic enzymes and characterized in comparison with MWL and kraft lignin. The residual lignin contained about 10% unremovable carbohydrates and was completely soluble in an alkaline solution and most of the lignin solvents. Elemental composition, molecular weight distributions, phenolic and aliphatic hydroxyl group contents and nitrobenzene oxidation products were examined in comparison with MWL and kraft lignin. The results showed that the residual lignin was found to have reacted to a lesser extent than the kraft lignin. Judging from these facts, the stable linkages between lignin and hemicellulose were suggested to exist in kraft pulp. The resistance of residual lignin to delignification was thus explained by the presence of these lignin-carbohydrate linkages.

Previously, it was suggested by Freudenberg et al.[2] that the benzyl ether linkage could be formed by the addition of hydroxyl groups in various monosaccharide units to quinonemethide intermediates during the biosynthesis of lignin. Later, Tanaka et al.[3] reported that even in the presence of water, the benzyl ether linkage was formed by the addition of C-6 hydroxyl group in glucose to quinonemethide which was synthesized from guaiacyl glycerol-β-guaiacyl ether. Furthermore, Leary et al. reported that the benzyl ether linkage was formed in the neutral aqueous solution of vanillyl alcohol and the sugars[4].

This summary suggest that benzyl ether types of lingin-carbohydrate complex (LCC) are present in wood. Some of these benzyl ether type LCC may be stable under alkaline pulping conditions and prevent complete delignification during chemical pulping.

In this paper, we sought to confirm the possibility of the presence of the lignin carbohydrate linkages which survive kraft cooking. For this purpose, a model compound of an α-ether type LCC was prepared and studied under alkaline as well as acid sulfite cooking conditions.

EXPERIMENTAL

Synthesis of Model Compounds

Quinonemethide

The quinonemethide of guaiacylglycerol-β-guaiacyl ether (GG) was prepared according to the method of Ralph et al.[5]. To a solution of 1.0 g GG (3.1 mM) in 30 ml chloroform was added 2.0 g of trimethylsilyl bromide (14 mM). The mixture was stirred for 2 hours at 0°C. The chloroform solution was transferred into a separatory funnel together with 30 ml saturated sodium bicarbonate solution and shakened. The chloroform layer which contained quinonemethide was separated and dried over anhydrous sodium sulfate.

Compound I

The chloroform solution of quinonemethide was poured into 20 ml dry DMSO solution containing 10 g of Methyl α-D-glucopyranoside (MαG) (52 mM) and the mixture was kept over night at room temperature. After the absence of quinonemethide was confirmed by the disappearance of a yellow color, chloroform was removed under reduced pressure. The residual DMSO solution was poured into 500 ml water and the aqueous mixture was extracted with 50 ml chloroform removal of GG and its condensation products and then extracted also with three portions of 100 ml ethyl acetate. After removal of ethyl acetate, a syrup was obtained which contained compound I and unreacted MαG. Compound I was purified with High Pressure Liquid Chromatography (HPLC).

High Pressure Liquid Chromatography (HPLC) analysis of Compound I showed four peaks (Fig. 1), and each of four isomers was separated and analyzed by C^{13} NMR. HPLC conditions were column, 20x250 mm; packing, CHEMCOSORB 70 DS-H; solvent, 22% acetonitrile in water; flow rate, 6 ml/min; and detector, UV-254. C^{13} NMR was determined in $(CD_3)_2CO$ using JEOL FX-100.

As shown in Table 1, the chemical shifts of C-α and C-6 in all four isomers of Compound I are 8 and 9 ppm, respectively, lower than those in GG and MαG, whereas the chemical shifts of all other carbons in compound I are similar to those of the corresponding carbons in GG and methyl-α-glucoside. Consequently, it is obvious that all four isomers of compound I have an ether linkage between the side chain C-α of lignin moiety and the C-6 of glucoside. The four isomers are formed due to the presence of the two chiral centers, C_α and C_β of side chain. However, it was not possible to identify each isomer based on these chemical shift data of C-13 NMR.

Compound II

Compound II was obtained from compound I (mixture) by methylation of phenolic hydroxyl group with diazomethane.

Compound III

Quinonemethide from GG was reacted with ethyl alcohol in the presence of sodium ethoxide and then the product was methylated with diazomethane to give Compound III.

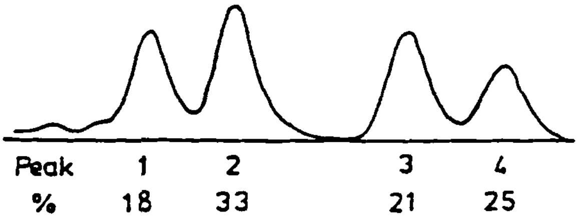


Figure 1. HPLC chart of Compound I detected with UV-254 nm

TABLE 1

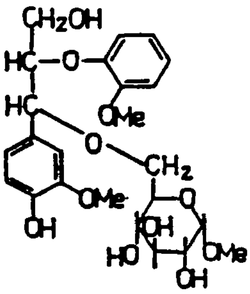
C-13 chemical shifts of four diastereoisomers of Compound I

Compound	C-γ	C-6	C-4	C-2	C-5	C-3	C-α	C-β
No. 1	61.1	68.8	70.8	71.8	72.5	74.3	81.8	83.6
No. 2	62.1	69.5	71.9	71.9	73.3	75.3	82.5	86.5
No. 3	61.8	69.2	71.5	71.9	73.0	74.9	82.0	84.8
No. 4	61.8	69.2	71.3	72.0	73.0	74.7	82.3	84.6
Me-glc		61.4	70.5	72.1	72.5	74.0		
GG e	60.8						72.8	87.1
t	61.0						73.1	84.6

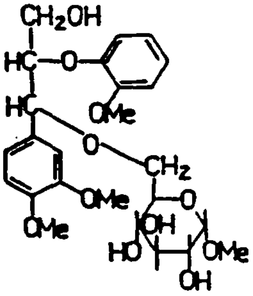
Me-glc: Methyl α-D-glucoside
GG: Guaiacylglycerol-β-guaiacyl ether
e: erythro
t: threo

Compounds IV and VG

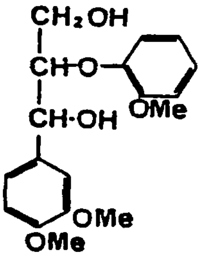
Veratrylglycerol-β-guaiacyl ether (VG) was synthesized by the method of Adler *et al.*[6]. Compound IV was synthesized from VG by the complete methylation with methyl iodide and NaOH in DMSO and purified by column chromatography.



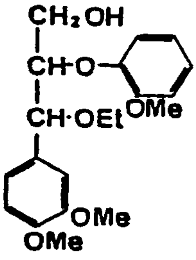
Compound I



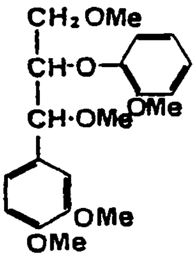
Compound II



VG



Compound III



Compound IV

Cooking

Soda cooking

Each model compound (6 mg) was dissolved in the mixture of 3 ml MeOH and 3 ml 2N NaOH solution respectively, and cooked at 160°C in a stainless steel autoclave. Reaction times were 30, 60, 90 and 120 minutes. After cooling, the reaction liquor was neutralized with 3 ml 2N HCl and diluted with MeOH to 25 ml. Compound II was cooked in various concentration of alkali (3 ml of 2, 4, 6 and 8N NaOH containing an equal volume of MeOH). Cooking temperature was 160°C for 1 hour.

Table 2

Recovery yields of VG in various ratios of MeOH

MeOH (%)	10	20	40	70	100
Yield (%)	45	44	47	43	38

Cooking Temperature: 160°C
Cooking Time: 30 min. with 1N-alkali

Cooking with various amounts of MeOH

In the present experiments, MeOH was necessary for dissolving the model compounds in cooking liquor. In order to access the effect of MeOH under alkaline pulping conditions, VG (10 mg) and NaOH (0.24 g) were dissolved in 6 ml of aqueous MeOH solutions and cooked at 160°C for 30 minutes. The MeOH concentrations were varied from 10-100%. As shown in Table 2, there is little difference in the recovery of VG in various concentrations of MeOH. Thus, the presence of Methanol does not affect the cooking results.

Kraft and acid sulfite cooking

Compound II was treated by kraft and acid sulfite liquors. Compound II (4.48 mg) was dissolved in 2 ml MeOH and 2 ml of the cooking liquor, and then cooked for 1 hour and 2 hours in a stainless autoclave. Cooking temperatures were 160°C and 135°C for Kraft and sulfite, respectively. The compositions of cooking liquor were: 34 g NaOH and 11 g Na_2S in 1 l of water, sulfidity 25% for kraft liquor with total SO_2 of 6.6% and combined SO_2 of 1.5% for acid sulfite liquor.

Analysis with HPLC

The reaction liquor was analyzed with HPLC, and the amount of the starting compound was determined for each cook. HPLC conditions were column, 3.9x300 mm; packing, μ-Bondapack C-18; solvent, 30% acetonitrile in water; flow rate of 1 ml/min; and detector; UV-280 nm and RI.

RESULTS AND DISCUSSION

Behavior of Compound I

Quantitative yield of MαG was obtained when compound I was cooked with 1N NaOH solution at 160°C for 15 minutes. Thus the α-ether in compound I was unstable and was cleaved completely in 15 minutes of the treatment. Other reaction products which were detected by GLC were identical to those which were obtained by the alkaline cooking of GG, that is, vanillin, acetoguaiacone and guaiacoxy styrene.

Cooking of Compound II

Table 3 shows the recovery percentage of Compound II under soda, kraft and sulfite cooking conditions. In the three types of cookings, Compound II was relatively stable, about 80% was recovered unchanged after two hours. There was only a small difference between the soda and the kraft cooking. This difference is probably due to the slight difference in alkali concentration between the two liquors since sulfide ions are expected to have no special effect on the stability of this compound[7,8]. Based on these results, soda cooking was adopted for further experiments instead of kraft cooking.

Behavior in soda cooking

The LCC model compound, compound II, was not as stable as MαG under soda cooking conditions as shown in Fig. 2. Compound III which has a benzyl-ethyl ether behaved similarly to compound II. Because MαG did not react at all, the loss of about 20% of compound II is not due to the degradation initiated by the sugar component but to a reaction starting from the side chain of the

TABLE 3

Recovery of Compound II after various cookings

	1 hour	2 hours
Soda	86%	72%
Kraft	91%	83%
Acid sulfite	86%	78%

Cooking temperature: 160°C, soda and kraft
135°C, acid sulfite

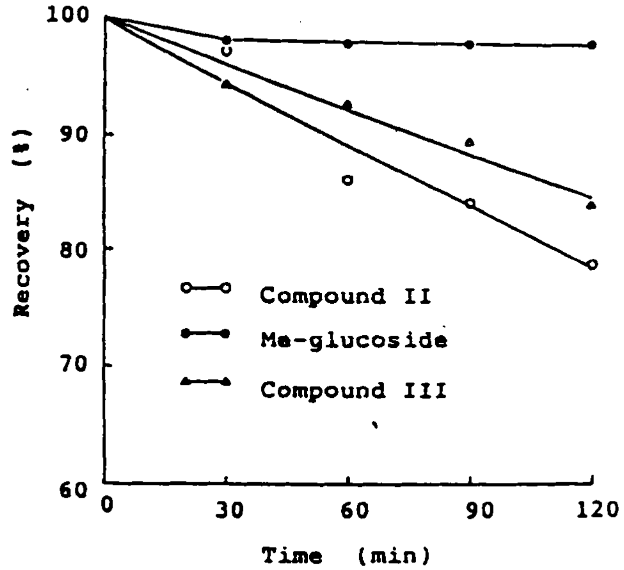


Figure 2. Recovery yields of unchanged model compounds after soda cooking. (cooking temperature of 160°C with 1N-alkali)

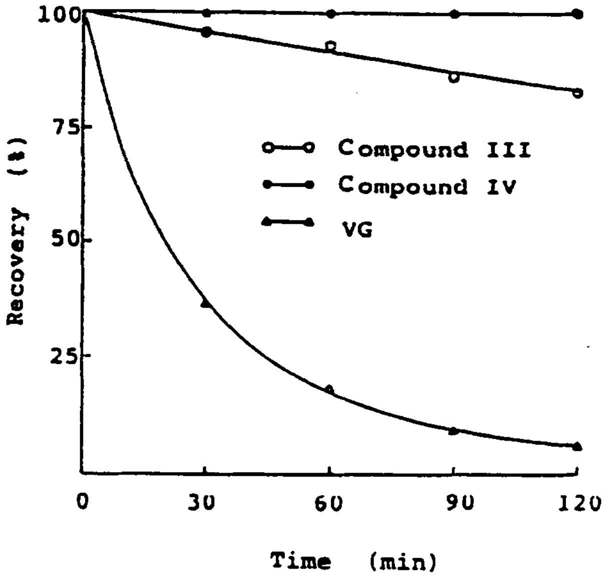


Figure 3. Recovery yields of unchanged lignin model compounds after soda cooking. (cooking temperature of 160°C with 1N-alkali)

phenylpropane unit. This is clearly demonstrated by the cooking results of lignin model dimers, compounds III and IV, which are shown in Fig. 3. Compound IV which has no hydroxyl group on the side chain was completely stable. On the other hand, VG which has two hydroxyl groups at the α and γ positions of the side chain reacted much more rapidly than Compound III with only one hydroxyl group. Thus, it is clear that the reactivities of these model compounds are related to the presence of hydroxyl group on the side chain and the 20% loss of Compound II is probably due to the cleavage of β-ether as a result of the dissociation of the hydroxyl group at γ-position, and the subsequent formation of an oxirane as proposed by Gierer and Noren[7].

The above mechanism is supported by additional experimental evidence showing that the stability of Compound II is a linear

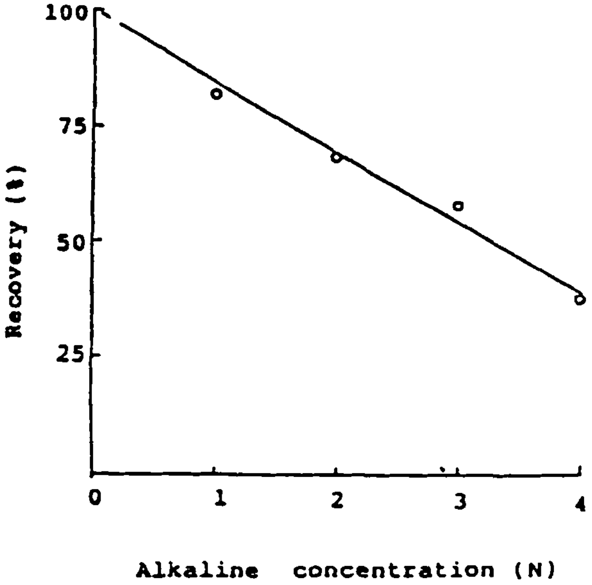


Figure 4. Degradation of Compound II in various concentration of alkali. (cooking temperature of 160°C with cooking time of 60 min.)

function of alkali concentration (Fig. 4). At higher alkali concentration, the increased dissociation of γ-hydroxyl group accelerates the degradation of compound II.

It should be noted that the 1 N and higher alkali concentrations used in the present study are much higher than those of normal kraft and soda pulping conditions. Although alkaline pulping processes normally start with alkali concentrations in the range of 40-50 g/l, over 50% of alkali charged is consumed during the heating up period as a result of polysaccharide degradation[9]. Consequently, the alkali concentration of the liquor when it reaches pulping temperature is considerably lower than 1 N. Thus, lignin carbohydrate linkages of non-phenolic α-ether type should be stable under kraft pulping conditions.

As shown in Fig. 3, VG, which has both α- and γ-hydroxyl groups is much less stable than Compound III, which has only γ-hydroxyl group, suggesting that the α-hydroxyl group may play a more important role in the neighboring group participating cleavage of β-ethers than the γ-hydroxyl groups. Thus, the presence of stable α-ether type lignin carbohydrate linkages may also retard the neighboring β-ether cleavage and thereby retard lignin degradation. This would explain our previous findings that the residual lignin in pulp is reacted to a lesser extent than the kraft lignin isolated from the black liquor[1].

Contrary to our results, Enoki <u>et al</u>. reported earlier that the lignin-carbohydrate linkages of the non-phenolic α-ether type were unstable under alkaline pulping conditions[10]. The contradiction is due to their improper choice of LCC model compound, which has a reducing end group in the carbohydrate moiety. It is well known that the reducing end group is very unstable under alkaline conditions and its reaction accounts for the instability of the model compound.

CONCLUSION

Based on our study of lignin model compounds, it can be concluded that non-phenolic α-ether type lignin-carbohydrate linkages are stable under alkaline and acid sulfite pulping conditions. The stable α-ether linkage also retards the cleavage of the neighboring β-ether linkage under alkaline pulping conditions. This may explain the resistance of the residual lignin in pulp to further delignification during kraft pulping.

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