

## Group B in Lignin \*

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Wood cannot be properly delignified by heating with normal sulphite cooking acid (pH 1—2) in the presence of reactive phenols such as resorcinol,  $\beta$ -naphthol, or pinosylvin. However, if the wood is first heated with sulphite solution with pH higher than about 4, delignification takes place during a subsequent normal sulphite cook at pH 1—2 even in the presence of such a phenol<sup>1</sup>.

To explain this Erdtman<sup>1</sup> assumed that lignin contains two groups possessing the following properties:

*Group A* 1: is sulphonated by acid, neutral and weakly alkaline sulphite solutions.

2: reacts at a higher rate with sulphite than with the phenols at a high pH.

3: reacts at a higher rate with the phenols than with sulphite at a low pH.

*Group B* 1: is sulphonated by sulphite solutions only at a low pH.

2: reacts, at all pH values, more slowly with phenols than with sulphite.

3: forms the linkage binding lignin in the wood. If the linkage is split, Group B is transformed into another group, termed *Group B'* (Erdtman<sup>2</sup>).

Since the sulphonation of all benzyl alcohols and benzyl ethers investigated is inhibited by phenols at a low pH and the inhibition decreases with increasing pH<sup>3-5</sup>, these substances exhibit the properties 2 and 3 in Group A above.

Of the same reason, benzyl alcohols and benzyl ethers do not possess property 2 in the scheme for the reactions of Group B.

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\* Part 49 on the chemistry of the sulphite process by E. Hägglund and co-workers. Part 48, *Acta Chem. Scand.* 5 (1951) 603.

That lignin is dissolved from sulphite pretreated wood despite of the presence of a reactive phenol depends on two factors. Firstly, the linkages<sup>6</sup> binding the lignin are split, and, secondly, the lignin product formed is soluble in water. Since the product is soluble, Erdtman<sup>1</sup> assumed that no condensation with phenols takes place and that Group B has the property described under Point 2. However, condensation products between ligninsulphonic acids and phenols can be soluble in water. Erdtman<sup>7</sup> has shown that if a "low sulphonated lignin" (= LSL) is heated with a normal sulphite cooking acid in the presence of resorcinol, the lignin product formed is soluble in water, despite the fact that the analyses show that it is a condensation product of the ligninsulphonic acid and resorcinol.

In order to investigate further the reactions of Group B in this respect, a LSL was heated with sulphite solutions of pH 1.2 and 2.3 in the presence of  $\beta$ -naphthol. Such a ligninsulphonic acid is obtained from wood which has been heated with sulphite solution of pH 5.2 at 135°, by dissolving the lignin by mild acid treatment<sup>7</sup>. Since Group A is sulphonated during the first step, the re-sulphonation of the LSL depends on Group B'. The LSL used contained 0.32 sulphur atom per methoxyl group. It was sulphonated (pH 1.1, 135°, 6 hours) to 0.52 sulphur atom per methoxyl group (Table 1).

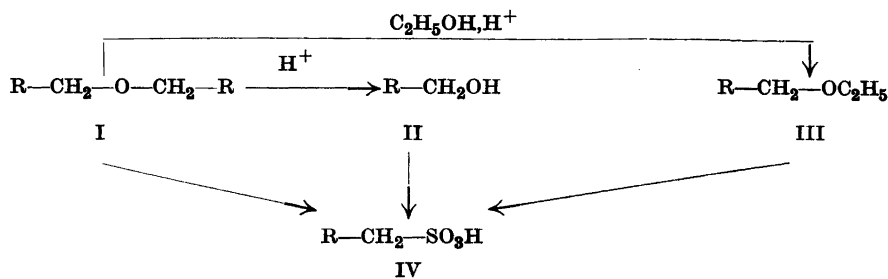
Table 1. The degree of sulphonation and condensation with  $\beta$ -naphthol at pH 1.2 and 2.3

Sulph. solution		Analyses of preparations obtained		
pH	$\beta$ -Naphthol with + without -	S/OCH <sub>3</sub>	C/OCH <sub>3</sub>	Condensed $\beta$ -naphthol per OCH <sub>3</sub> *
	LSL	0.35	10.4	—
1.2	+	0.35	13.4	0.30
2.3	+	0.42	11.0	0.06
1.1	—	0.52	—	—

\* Calc. from the ratio C/OCH<sub>3</sub>.

The addition of  $\beta$ -naphthol completely prevented sulphonation of LSL at pH 1.2 (Table 1). The C/OCH<sub>3</sub> ratio showed that  $\beta$ -naphthol had combined with the lignin in the ratio of 0.30 mole of  $\beta$ -naphthol per methoxyl group of lignin. At pH 2.3, Group B' is partly sulphonated despite the presence of  $\beta$ -naphthol. Thus, *in the competitive reactions with sulphite and phenols Group B' reacts as a benzyl alcohol or benzyl ether group.*

Fig. 1. Diveratryl ether as a lignin model.



R = 3,4-dimethoxy-phenyl-

The preparations obtained were soluble in water. For that reason the dissolution of the lignin from sulphite treated wood by a normal sulphite cooking acid in the presence of a reactive phenol is probably due to the splitting of the linkages which bind the lignin in the wood, and to the formation of a soluble condensation product of the ligninsulphonic acid and the phenol. The pretreatment with a sulphite solution of high pH results in sulphonation to such a degree that the phenol condensation product obtained in the second stage becomes water soluble.

Apart from the competitive reactions between sulphite and phenol, the following is known about the Group B and B'.

(i) The acetylation of ligninsulphonic acids of varying sulphur content has shown that the hydroxyl content decreases on sulphonation. For that reason Group B' is evidently a hydroxyl group<sup>8</sup>.

(ii) If sulphite treated wood is heated with ethanolic hydrochloric acid, ethoxyl groups are introduced into the ligninsulphonic acid. If these ethylated ligninsulphonic acids are then re-sulphonated, the ethoxyl groups are eliminated as ethanol. This reaction sequence can be most easily explained by assuming that ethylation of lignin takes place at the same group as the sulphonation — that is Group B<sup>9</sup>.

(iii) Benzyl aryl ether groups can be sulphonated<sup>10,11</sup>, thereby giving rise to phenolic groups, but as ligninsulphonic acids contain only few phenolic groups the sulphonation of lignin may not to any large extent be due to such groups<sup>12-14</sup>. For that reason Group B may not be a benzyl aryl ether group.<sup>12</sup>

Points 1 and 3 as well as (i)—(iii) are satisfied, at least in a qualitative sense, by the model substance diveratryl ether<sup>5</sup> (I, the Fig. 1). On heating with a normal sulphite cooking acid at 135°, this is rapidly transformed into 3,4-dimethoxy-toluene- $\omega$ -sulphonic acid (IV). At pH 5 it is sulphonated only slowly, and at pH 6 and higher, no reaction takes place. The rate of hydrolysis

of the dibenzyl ether linkage of diveratryl ether by sulphite solutions of varying pH is rather similar to the rate of dissolution of lignin in the same reagents<sup>15</sup>. Diveratryl ether reacts with ethanolic hydrochloric acid to give veratryl ethyl ether (III): the latter reacts with sulphite cooking acid, with the elimination of the ethoxyl group and formation of the sulphonic acid IV<sup>5</sup> (cf. Holmberg's theory for the formation of ethanol lignin<sup>16</sup>).

Consequently, there is much evidence in favour of the view that Group B is a *para*- (or *ortho*-) alkoxy-benzyl ether group. From that follows that Group B' is the corresponding substituted benzyl alcohol.

### EXPERIMENTAL

(Microanalyses by W. Kirsten)

All values are calculated on a salt free basis. The pH determinations are carried out at room temperature.

1) 1.39 g of a "low sulphonated lignin" ( $C_9H_{8.3}O_{2.6}(OCH_3)_{0.95}(SO_3H)_{0.33}$ ) dissolved in a sulphite solution (50 ml, 5 %  $SO_2$ , 0.8 % NaOH, pH 1.2).  $\beta$ -Naphthol (0.43 g) was added and the mixture was then heated for 6 hours at 135° in a rotating stainless steel tube.

The solution was extracted with benzene (3 × 25 ml), and the extract dried over anhydrous sodium sulphate, and evaporated. A red oil (0.26 g) was obtained which on vacuum sublimation yielded  $\alpha$ -naphthol (0.14 g).

The aqueous solution was dialysed with water until free from sulphate and sulphite ions, and then evaporated to dryness in *vacuo*. The residue weighed 0.86 g.

2) The second experiment was carried out as above, but with the variation that the pH of the sulphite solution was 2.3.

3) The third experiment was carried out as the first one but with the variations that no  $\beta$ -naphthol was added and the extraction with benzene was omitted.

The results are shown in Tables 1 and 2.

Table 2. The yield and analyses of the lignin preparations obtained.

pH	$\beta$ -Naphthol with + without -	Recovered $\beta$ -naphthol g	Lignin preparations obtained				
			Amount g	Yield of $OCH_3$ , %	S, %	$OCH_3$ , %	C, %
	LSL		—	—	4.97	13.8	56.0 *
1.2	+	0.19	1.03	63	4.30	11.8	61.4
2.3	+	0.33	1.15	80	5.77	13.4	57.1
1.1	—	—	0.86	60	7.17	13.3	—

\* H 5.28 %.

## SUMMARY

1. A "low sulphonated lignin" has been treated at 135° with sulphite solutions of pH 1.2 and 2.2 in the presence of  $\beta$ -naphthol.

2. It is suggested that Group B is an *ortho*- or *para*-alkoxybenzyl alkyl ether group.

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## REFERENCES

1. Erdtman, H. *Svensk Papperstidn.* 43 (1940) 255, *Cellulosechemie* 18 (1940) 83.
2. Erdtman, H. *Research* 3 (1950) 83.
3. Lindgren, B. O. *Acta Chem. Scand.* 3 (1949) 1011.
4. Erdtman, H., and Leopold, B. *Acta Chem. Scand.* 3 (1949) 1358.
5. Lindgren, B. O. *Acta Chem. Scand.* 4 (1950) 1365.
6. Hägglund, E. *Holzchemie*, Leipzig (1938) p. 152.
7. Erdtman, H. *Svensk Papperstidn.* 48 (1945) 75.
8. Erdtman, H., Lindgren, B. O., and Pettersson, T. *Acta Chem. Scand.* 4 (1950) 228.
9. Erdtman, H., and Pettersson, T. *Acta Chem. Scand.* 4 (1950) 971.
10. Freudenberg, K., Meister, M., and Flickinger, E. *Ber.* 70 (1937) 500.
11. Richtzenhain, H. *Ber.* 72 (1939) 2152.
12. Freudenberg, K., Lautsch, W., and Piazzolo, G. *Cellulosechemie* 22 (1944) 97.
13. Aulin-Erdtman, G. *Tappi* 32 (1949) 160.
14. Richtzenhain, H. *Svensk Papperstidn.* 53 (1950) 647.
15. Lindgren, B. O. *Acta Chem. Scand.* 5 (1951) 613.
16. Berg, G. A., and Holmberg, B. *Svensk Kem. Tid.* 47 (1935) 257.

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