

## Pinoresinol as a Lignin Model \*

BENGT O. LINDGREN and ULLA SAEDÉN

*Department of Wood Chemistry and Cellulose Technology, Royal Institute of Technology, Stockholm, Sweden*

A great deal of work has been carried out to see if substituted benzyl alcohols are appropriate lignin models, and it has been shown that in several respects these alcohols do indeed resemble the sulphite-reacting groups present in lignin <sup>1-5</sup>. However, the benzyl alcohols hitherto investigated react too rapidly with neutral sulphite solutions to be close analogues of the less reactive of the sulphonatable groups in lignin — the groups B <sup>6</sup>.

Recently, therefore, we investigated the reactivity of a model substance (diveratryl ether) containing benzyl alkyl ether residues towards, *inter alia*, sulphite solutions of various degrees of acidity <sup>5</sup>. It appeared from the results obtained with this model that the groups B might possibly be of the *p*-alkoxybenzyl alkyl ether type <sup>7</sup>.

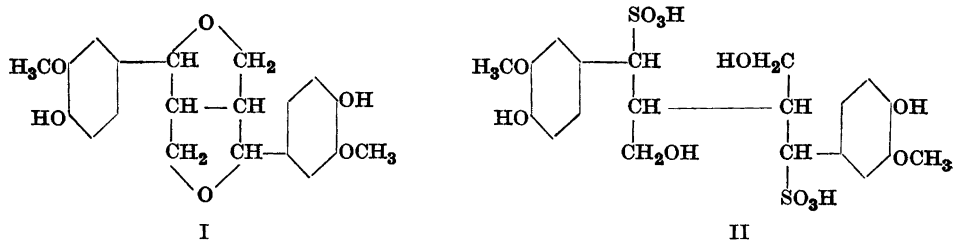
It then occurred to us that the more reactive of the sulphite-reacting groups — groups X and Z <sup>8</sup> — might be some other type of benzyl alkyl ether groups. Both groups X and Z are sulphonated in neutral solution (X rapidly and Z slowly) so that it was necessary to search for a benzyl alkyl ether that is sulphonated under these conditions.

Sulphonation experiments with benzyl alcohols have shown that *p*-alkoxybenzyl alcohols are sulphonated considerably more readily than *p*-alkoxybenzyl alcohols <sup>2</sup>, especially by neutral or faintly alkaline sulphite solutions, so that it appeared that a *p*-hydroxybenzyl alkyl ether structure would have the desired properties.

Groups of this type occur in several of the lignans (natural products built up from two phenyl propane units) such as, for example, pinoresinol (I). Erdtman <sup>9</sup> has studied the action of acidic sulphite solutions on this substance, and showed that pinoresinol does not dissolve in such solutions (pH 1.5—2)

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\* Part 51 on the chemistry of the sulphite process by E. Hägglund and coworkers. Part 50, *Svensk Papperstidn.* 54 (1951) 795.



at 135°, but is converted into an insoluble condensation product which is almost free of sulphur. Consequently the major portion of the benzyl ether groups in the pinosresinol had not been sulphonated. Similar experiments with dimethyl and diethyl ethers of pinosresinol showed that these structures are not sulphonated under the same conditions<sup>9</sup>.

Earlier researches have shown that the sulphonation of benzyl alcohols<sup>2,3,5</sup> and of diveratryl ether<sup>5</sup> is suppressed by phenols at pH 1–2 and that this effect diminishes with increasing pH. As pinosresinol itself contains phenolic hydroxyl groups which may hinder the sulphonation, it seemed possible that pinosresinol could be sulphonated at pH's higher than those employed by Erdtman. We have, therefore, investigated the reaction between pinosresinol and sulphite solutions of various degrees of acidity.

When pinosresinol was heated with sulphite solutions of various pH at 135° for 45 minutes we obtained the following results (Table 1):

At pH 2, we found, as did Erdtman, that most of the pinosresinol was converted into an insoluble condensation product.

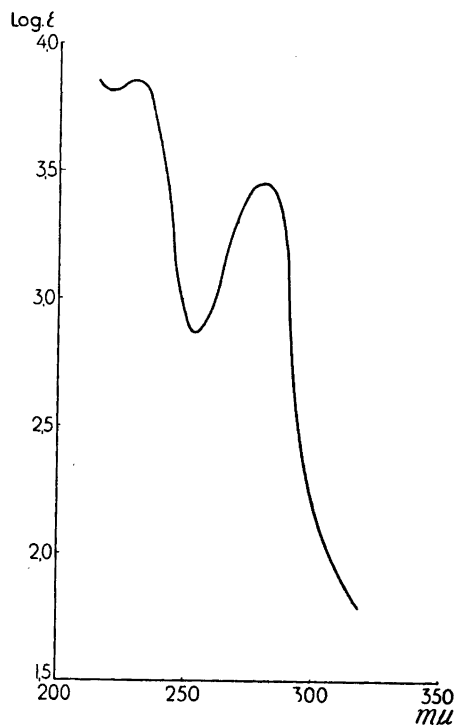
At pH 4, approximately 60% of the pinosresinol dissolved, the remainder being converted into an insoluble condensation product.

At pH 6, 8, and 10, the pinosresinol dissolved almost completely in the sulphite solutions.

From the sulphite solution obtained from an experiment using neutral sulphite solution heated at 135° for 1.5 hours we isolated an amorphous

Table 1. Pinosresinol dissolved after treatment with sulphite solutions of varying pH for 45 minutes at 135°.

pH	2	4	6	8	10
Pinosresinol dissolved, %	18	64	97	99	93



*Fig. 1. The ultra-violet absorption curve of sulphonated pinoresinol.*

product in a yield which accounted for 57 % of the methoxyl content of the starting material. The ultra-violet absorption curve (Fig. 1) exhibited the characteristics expected for an aromatic compound with no double bond conjugated with the benzene ring.

The water-solubility, sulphur content and ash content showed that the product contained sulphonic acid groups and, on analogy with the sulphonation of diveratryl ether, these must have been formed by the sulphonation of the benzyl ether groups. However the product contained appreciably less sulphur and more methoxyl than the structure II which would be the expected product from the sulphonation of pinoresinol. It appears that not all of the benzyl ether groups of the pinoresinol had been sulphonated and as even prolongation of the time of heating to 3 hours (compared with 1.5 hours) gave a product which showed the same deviation from the expected structure II, the remainder of the benzyl ether groups must have undergone condensation under the influence of the sulphite solution.

After this work was completed, Leopold (private communication) sulphonated pinoresinol and obtained a product, the composition of which agreed

Table 2. *Pinoresinol dimethyl ether dissolved (in percent) after treatment with sulphite solutions of varying pH, for various lengths of time at 135°.*

Time, hours	pH					
	2	3	4	5	6	11
2	15	5				
13		15				
20			8*	9*	8*	0*

\* The dimethyl ether was recovered in crystalline form.

much better with the structure II than that of the material described above. Leopold used a larger ratio of sulphite solution to pinoresinol than we employed, and his material (the barium-salt) contained 8.37 % S and 9.07 % methoxyl (calculated for barium-salt of II, 9.74 % S and 9.43 % methoxyl).

Sulphite cooking of pinoresinol has shown, therefore, that *p*-hydroxybenzyl ether groups which are sulphonated in neutral solution as rapidly as the groups X in lignin do indeed exist. In a preliminary note in Part 48 of this series<sup>8</sup> we pointed out that the groups X might be of this type. At the same time, however, we also pointed out that there is another possibility, namely that these lignin groups may be *p*-hydroxybenzyl alcohol groups.

We have also investigated the reaction of pinoresinol dimethyl ether with sulphite solutions of various pH, and confirmed the findings of Erdtman<sup>9</sup> that at low pH the dimethyl ether is not sulphonated to any greater extent (Table 2). As the ether is transformed into an amorphous product in this pH-region it has probably condensed. At pH 4 and above the ether neither condenses nor sulphonates, but is recovered unchanged.

That the *p*-alkoxybenzyl ether groups in pinoresinol ethers, unlike those in diveratryl ether, are not sulphonated but undergo condensation under the action of acid sulphite solutions, is probably due to the sparing solubility in water of the former. Because of the insolubility it is more difficult for the sulphite ions to react with the model substances. The condensation reaction, however, is not hindered to the same extent because of the mobility of the hydrogen ions.

#### EXPERIMENTAL

A mixture of pinoresinol (1 g) and a solution of sodium sulphite (10 ml, 5 % total SO<sub>2</sub> adjusted to pH 7 with NaOH) was heated in a rotating glass tube at 135° for 1.5 hours, during which time the pinoresinol dissolved almost completely. Sodium ions were remov-

ed by passage through a cation exchanger and the sulphur dioxide expelled by a stream of nitrogen. The solution was neutralised with barium hydroxide, filtered, and evaporated *in vacuo* and the residue (1.47 g) dissolved in a little water. An equal volume of isopropyl alcohol was added, the precipitated barium sulphite filtered off and the product precipitated by the addition of acetone and ether. This material (1.05 g) contained neither sulphate nor sulphite ions.

$C_{20}H_{24}O_{12}S_2Ba$ (formula II)	Calc.	OCH <sub>3</sub>	9.4	S	9.7
	Found	»	11.2	»	6.4

The ultra-violet absorption curve of the material is shown in Fig. 1.

The results listed in Tables 1 and 2 were obtained by heating the model substances with sulphite solutions in the same way as was used for the corresponding determinations on diveratryl ether and veratryl alcohol<sup>5</sup>.

#### SUMMARY

Pinoresinol has been sulphonated by sulphite solutions at pH 6—9.

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