

## Treatment of Spruce Lignin with Sulphite Solutions at pH 4—9\*

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According to Hägglund<sup>1</sup> the dissolution of lignin during the sulphite process takes place in two steps. The first step involves the sulphonation of the lignin, the other a hydrogen catalysed splitting (probably a hydrolysis) of linkages binding the lignin in the wood.

In order to study further these two steps, extracted wood powder (spruce, *Picea abies* (L.) Karst.) has been heated at 135° with sulphite solutions, for times varying from 1 to 24 hours, and at pHs varying from 4 to 9. (All pH values reported in this paper are determined at room temperature.) The sulphite treated wood powders were then analysed for lignin and sulphur.

The methoxyl content of the wood powders has been used as a measure of the lignin content. Eighty-nine percent of the methoxyl groups of the extracted wood are found in the Klason lignin. If no methoxyl groups are split off from the lignin during the isolation of Klason lignin, eleven percent of the methoxyl groups are bound to the carbohydrates (*cf.* Hägglund and Sandelin<sup>2</sup>). The methoxyl estimation consequently gives values for the lignin content which are too high. For this reason, in some cases, spectrophotometric determinations of the amounts of dissolved lignin have been used as a complement to the methoxyl determinations.

Sulphur has been determined by a modification of the Grote-Krekeler method<sup>3</sup>, which allows a more rapid analysis of samples containing sodium salts.

The discussion of these experiments has been divided into two parts. The first deals with the sulphonation of the undissolved lignin, and the second with the splitting of the linkages binding lignin in the wood.

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\* Part 48 on the chemistry of the sulphite process by E. Hägglund and coworkers.  
Part 47 *Acta Chem. Scand.* 4 (1950) 971.

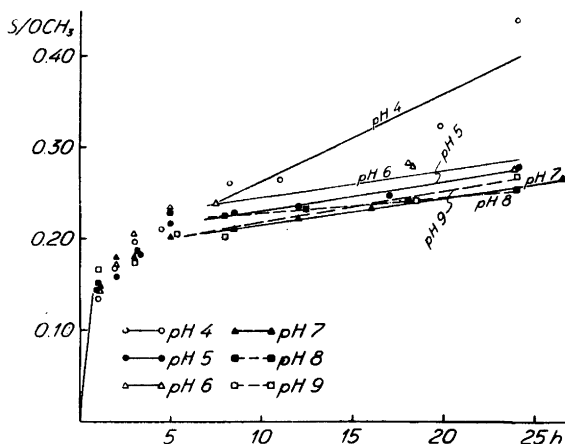


Fig. 1. The ratio of sulphur atoms per methoxyl group of the sulphite treated wood as a function of heating time at 135° for sulphite solutions of different pH.

#### THE SULPHONATION OF UNDISSOLVED LIGNIN

Hägglund and Johnson<sup>4</sup> heated wood powder with an almost neutral sulphite solution (pH 6) at 135°. The greater part of the lignin remained in the wood after this treatment. After 30 hours heating the wood contained 0.33 sulphur atom per methoxyl group. Most of the sulphur (0.22 atom per methoxyl group) was taken up during the first 5 hours. If the heating was continued for longer than 30 hours no more sulphur was taken up.

From these results Hägglund and Johnson concluded that the sulphonation of lignin takes place in two steps. The lignin is first rapidly sulphonated until it contains 1 sulphur atom per 4 methoxyl groups. A considerably slower sulphonation then follows.

The results of the present investigation show that the wood takes up 0.25—0.28 sulphur atom per methoxyl group during 24 hours heating at 135° with a sulphite solution having a pH between 5 and 9 (see Fig. 1). At pH 4, 0.44 sulphur atom per methoxyl group have been taken up after 24 hours heating, but under these conditions the greater part of the lignin is dissolved. This value can, therefore, not be compared with those obtained at pH 5—9 because, in those cases, not more than a third of the lignin is dissolved during 24 hours heating (see below).

A considerable part of the sulphur (0.13—0.17 sulphur atom per methoxyl group) is bound during the first hour. If the final portions of the curves in Fig. 1 are extrapolated to time 0, it is found that 0.18—0.22 sulphur atom per methoxyl group is rapidly taken up.

When wood is heated with sulphite solution, part of the sulphur may be bound as loosely bound sulphite, *i. e.* sulphite which can be liberated by alkali at room temperature. (This sulphite is mainly bound to carbonyl groups <sup>5</sup>). When the sulphonated wood powder was treated with alkali, the sulphur content was reduced by 0—0.03 sulphur atom per methoxyl group. The formation of loosely bound sulphite is consequently of little quantitative importance when wood reacts with sulphite solutions of pH 4—9.

In order to investigate the initial rapid sulphur uptake, the lignin was isolated as hydrochloric acid lignin (by Richtzenhain's method <sup>6</sup>) from wood powders which had been obtained by heating the wood for one hour with the sulphite solutions. As mentioned above, these woods contained 0.13—0.17 sulphur atom per methoxyl group. The hydrochloric acid lignin preparations contained 0.12—0.16 sulphur atom per methoxyl group (see Table 1), and this shows that the rapid sulphur uptake during the first hour of heating is due to the sulphonation of lignin. (Vanillyl alcohol is the only model substance hitherto studied which reacts as rapidly as lignin under these conditions <sup>7</sup>).

Table 1. The preparation of hydrochloric acid lignin from wood powders treated with sulphite solutions of different pH at 135° for 1 hour.

pH of sulph. solut.	Yield of hydrochloric acid lignin		Analysis of the hydrochloric acid lignin			Ratio S/OCH <sub>3</sub> in the wood
	Weight %	Methoxyl %	Sulphur %	Methoxyl %	S/OCH <sub>3</sub>	
4	27.2	75	1.63	13.5	0.12	0.13
5	26.4	73	1.72	13.0	0.13	0.15
6	25.3	74	1.87	13.8	0.13	0.14
7	24.7	73	2.18	14.5	0.15	0.15
8	25.1	72	2.41	14.4	0.16	0.15
9	24.9	75	2.18	14.7	0.14	0.17

From a sulphonated wood powder, prepared by heating wood with sulphite solution at pH 5.2 and 135°, containing about 0.3 sulphur atom per methoxyl group, a large part of the lignin could be removed by heating in acid solutions (see Scheme 1). The dissolved lignin ("low sulphonated lignin" = LSL) contained about 0.3 sulphur atom per methoxyl group <sup>8</sup>. Thus the slower sulphonation during which the sulphur content increases from 0.18—0.22 0.25—0.28 sulphur atom per methoxyl group is probably due to the sulphonation of lignin.

Note added in proof (Mai 12, 1951). Mikawa and co-workers (private communication) have recently investigated the sulphonation of *Picea jezoensis* and *P. densiflora* at 135° and pH 6. They too assumed that this sulphonation is a two-step reaction — a rapid sulphonation followed by a slower one. The groups which react rapidly they called Groups X and those which react slowly Groups Z. Erdtman had earlier called all the groups which are sulphonated at pH 6 Groups A.

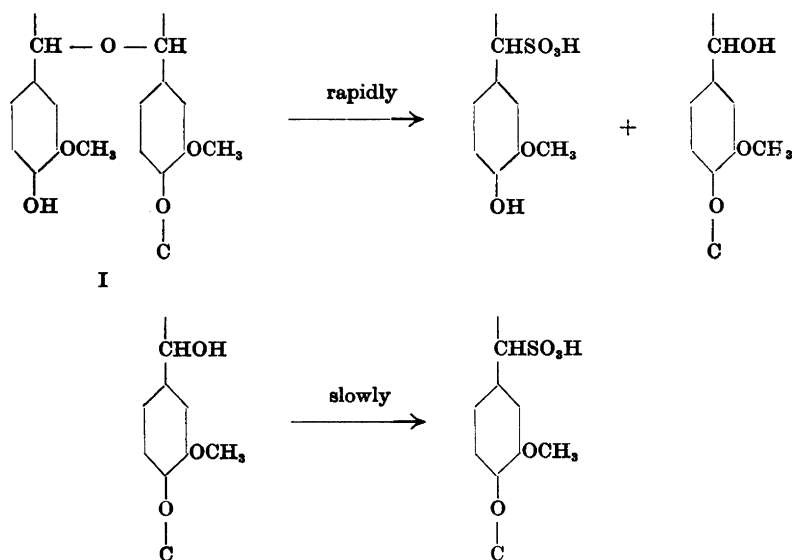
In this paper it has been stated that vanillyl alcohol is the only model substance investigated which is sulphonated as rapidly as Groups X. However, Lindgren and Sædén have recently found that pinoresinol also reacts as rapidly as Groups X with neutral sulphite solutions. Thus Groups X may be *p*-hydroxyl-benzyl alcohol groups (as in vanillyl alcohol) or *p*-hydroxyl-benzyl ether groups (as in pinoresinol).

As the Groups Z are sulphonated at a rate which is of the same order of magnitude as the rate of sulphonation of model substances containing *p*-alkoxy-benzyl alcohol groups, Groups Z may be groups of this type.

Groups X and Z can be combined in a simple way to one type of group, having the formula I. During sulphonation at pH 6, the phenol activated part of such a group is rapidly sulphonated. In this process a *p*-alkoxy-benzyl alcohol group is formed, and this group then is sulphonated slowly under these conditions.

If all the Groups X and Z (= Groups A) have the formula I, the lignin must contain the same amounts of Groups X as Groups Z. Mikawa and co-workers found this to be the case in the lignins of the spruces they investigated. On the other hand in this paper it is assumed that the lignin of *Picea abies* contains more Groups X than Groups Z. This may be explained by assuming that some of Groups X of *P. abies* lignin are etherified by other Groups X or by hydroxyl groups which can not be sulphonated.

In Part 49 of this series, it is shown that the groups in lignin which are sulphonated at pH about 1.5–2 but not at pH 6 (Groups B) may be benzylether groups and thus all the lignin groups which are responsible for the sulphonation reactions may be benzyl ether groups.



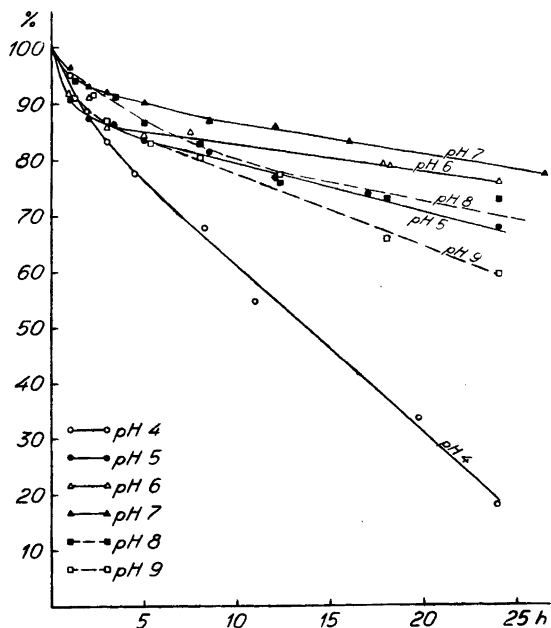


Fig. 2. The number of methoxyl groups of the sulphite treated wood (expressed as the percentage of the number of methoxyl groups of the original wood) as a function of the heating time at 135° for sulphite solutions of different pH.

THE SPLITTING OF THE LINKAGES BINDING LIGNIN IN THE WOOD

In Fig. 2 the number of methoxyl groups in the sulphite treated wood powder, expressed as the percentage of the number of methoxyl groups in the original wood powder, has been plotted as a function of the heating time for sulphite solutions of different pH.

Table 2. The number of lignin-bound methoxyl groups (expressed as the percentage of the number of lignin-bound methoxyl groups in extracted wood) dissolved by treating the wood with sulphite solutions of varying pH at 135° for 4 hours.

pH of sulphite solut.	4.9	5.3	5.8	6.2	6.7	8.0
Amount of dissolv. lignin, %	16.5	17.1	12.0	11.4	14.7	17.6

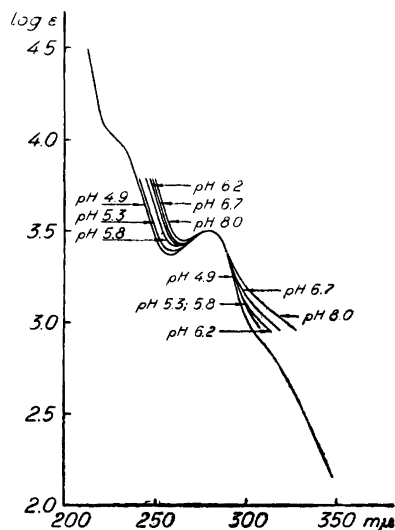


Fig. 3. The ultra-violet absorption curves of the lignin which is dissolved by heating the wood with sulphite solutions of pH 4.9 to 8.0 at 135° for 4 hours. The curves have been displaced along the ordinate so that the maximum at 280  $m\mu$  lies at  $\log \epsilon = 3.5$ .

The first, rapid dissolution of methoxyl at pH 6 and 7 (see Fig. 2) is due to dissolution of lignin. This was shown by spectrophotometric determinations of the amount of lignin which has passed into solution after 4 hours heating (see Table 2). Thus, only 11—15 percent of the lignin is rapidly dissolved by sulphite solutions at pH 6—7, the bulk remaining in the wood.

Fig. 3 shows the absorption curves of the different solutions obtained by these treatments. The form of the curves varies in a regular way with the pH of the sulphite solutions.

A large part of the lignin of the sulphite treated wood is dissolved if the wood is heated with acids<sup>4,8</sup> (see Scheme 1). When buffered solutions of varying pH are employed, the rate at which the lignin dissolves increases with the hydrogen ion concentration<sup>9</sup>. This shows that the bulk of the lignin is bound by linkages the splitting of which is catalysed by hydrogen ions (Hägg-lund<sup>1</sup>).

The small fraction of the lignin which is rapidly dissolved at pH 6—7 cannot be bound in this way. This fraction has neither been isolated nor studied.

Some investigations have previously been carried out on a similar fraction the "low molecular ligninsulphonic acid" (= LMLA, see Scheme 1). This fraction is dissolved when wood is heated at 135° with a sulphite solution of pH 5.2<sup>10</sup>, and it comprises about one third of the lignin of the wood.

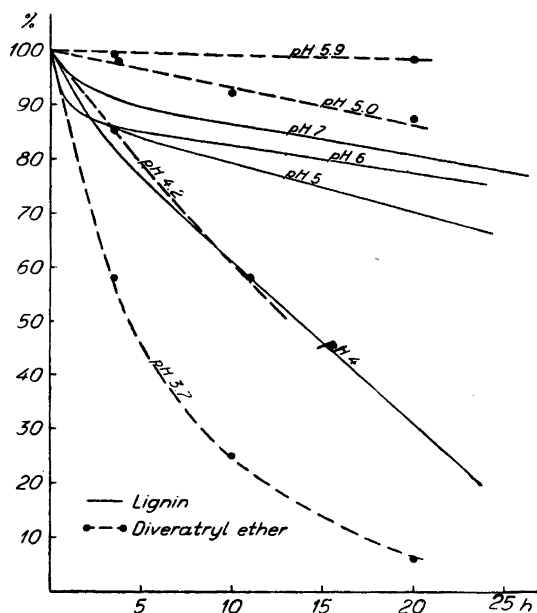


Fig. 4. The amount of diveratryl ether recovered, after heating at 135° with sulphite solutions, as a function of the heating time at different pH. For comparison, the curves of Fig. 2 for the dissolution of lignin are plotted in the figure.

LMLA seems to be sulphonated to a higher extent (probably about 0.5 sulphur atom per methoxyl group) than the fraction of lignin which remains in the wood (0.3 sulphur atom per methoxyl group), and the molecular weight is lower than that of the LSL<sup>10</sup>.

As mentioned above, at pH 6—7, the linkages which bind the bulk of the lignin are not split to an appreciable extent. The fact that the lignin is dissolved more quickly and in greater amounts at lower pH implies a splitting of these linkages.

The rate-determining factor for the dissolution of the bulk of the lignin at a pH just below 6 is therefore, probably, the rate of the splitting of these linkages. The pH range seems to extend to at least pH 4 because the rate of dissolution of the lignin in the pH range 4—6 is strongly pH dependent, indicating that the rate is determined by a hydrogen ion catalysed reaction.

Heating with alkaline solutions dissolves the lignin more quickly and to greater extent than heating with sulphite solutions of pH 6—7 (see Fig. 2). This cannot of course be explained by the hydrogen ion catalysed reaction.

Many investigators have assumed that lignin is bound in the wood by acetal linkages because of the acid-labile nature of such linkages<sup>11,12</sup>. On the

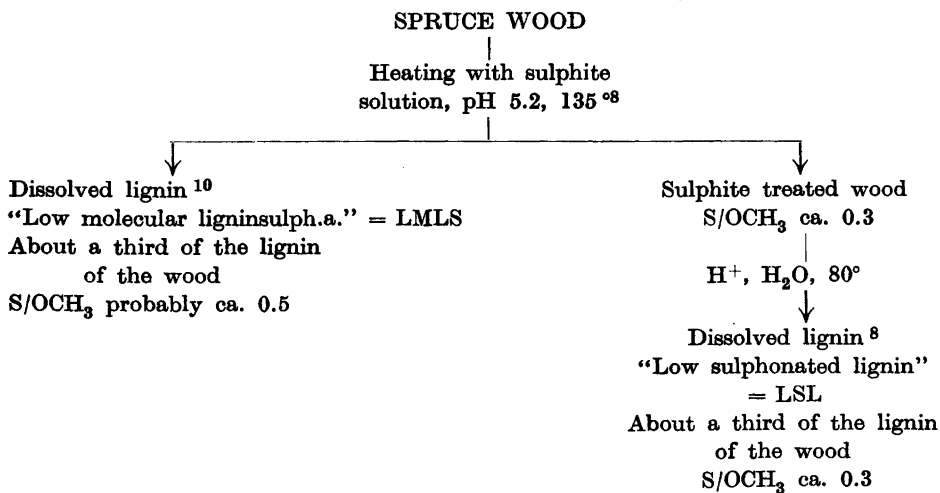
other hand Holmberg<sup>13</sup> has assumed that these linkages are of the benzyl ether type. Such ethers are hydrolysed much more easily than ordinary ethers.

In a recent communication<sup>14</sup> the sulphonation of diveratryl ether (3,3', 4,4'-tetramethoxy-dibenzyl ether) was studied at different pHs. It was found that diveratryl ether disappears from the reaction mixture at a higher rate than the sulphonic acid is formed. This indicates that the sulphonation proceeds via an intermediate product, most probably veratryl alcohol. In Fig. 4 the amount of recovered diveratryl ether is plotted as a function of the time of heating, at different acidities of the sulphite solution. The figure shows that the rate of hydrolysis of the ether linkage is rather similar to the rate of solution of the lignin using sulphite solutions of a pH lower than 7. This indicates that alkoxy-benzyl alkyl ether linkages may be responsible for binding the bulk of the lignin in wood\*.

The mechanism of the dissolution of lignin in alkaline sulphite solutions cannot be studied using diveratryl ether as a model substance, as this ether is not hydrolysed by this reagent.

From the above it may be concluded that lignin in the native state is built up of units containing a number of C<sub>9</sub>-monomers. The units are coupled together or with carbohydrate molecules by means of benzyl ether linkages.

*Scheme 1. Preparations obtained by treating spruce wood with sulphite solution at pH 5.2 and 135°.*



\* The above mentioned experiments with pinoresinol show that the fraction which is easily dissolved at pH 6-7 may be bound with *p*-hydroxy-benzyl ether linkages (added in proof).



This hypothesis is supported by the fact that several lignans contain this type of grouping. Further, since *p*-methoxy-benzyl alcohols undergo etherification even at room temperature<sup>14,15</sup> these linkages could be formed by direct etherification of benzyl alcohol groups in a protolignin.

It is probable that the lignin units just mentioned are built up from only a few  $C_9$ -monomers, since lignin preparations isolated by a mild method have a molecular weight of the order of 1 000<sup>16</sup>; corresponding to about 5  $C_9$ -monomers.

In a recent paper Stumpf and Freudenberg<sup>17</sup> reported that they have succeeded in dissolving the lignin of spruce wood under very mild conditions. They found no indications of a chemical linkage between the lignin and the carbohydrates of the wood, and considered that the union must be by hydrogen bonding.

## EXPERIMENTAL

### Sulphur determination

The sample of sulphite treated wood powder (0.7 g) weighed into a platinum boat was combusted in the usual way in a Grote-Krekeler apparatus<sup>3</sup>. The sulphuric acid formed was determined by titration with 0.1 N NaOH.

The sodium content of the wood powder caused the formation of ash containing sodium sulphate and sodium carbonate. The amount of sodium carbonate in the ash was determined by titration with 0.1 N HCl (bromophenol blue as indicator), and the remainder was assumed to be sodium sulphate. The amount of sulphur in the sample thus becomes the sum of the amounts of sulphur in the sodium sulphate and the sulphuric acid.

The values obtained for the amount of sulphur in the ash were checked for certain samples by precipitating the sulphate in the titrated solution as  $BaSO_4$ . The difference between the determination were less than 1 % — an accuracy sufficiently great for this investigation.

### Treatment of the wood powder with sulphite solutions

The wood powder (spruce, *Picea abies*) was extracted for 24 hours with ethanol-benzene (1 : 1). The extracted wood powder contained 4.99 % methoxyl and 28.8 % Klason lignin having a methoxyl content of 15.5 %.

The sulphite solutions were prepared by dissolving sulphur dioxide and sodium hydroxide in water in such amounts that the total content of sulphur dioxide was 5 %, and the pH of the solution had the desired value (4, 5, 6, 7, 8, or 9).

The extracted wood powder (25 g) was mixed with the sulphite solution (300 ml) in an acid-resistant steel autoclave, which was then rotated for the desired time in an oil bath at 135°.

The wood powder was then filtered off and the pH of the solution was determined. The product was thoroughly washed (several days) with water until the filtrate did not contain sulphite or sulphate ions, and determinations were then made of the yield (Fig. 5), the methoxyl content (Fig. 6) and the sulphur content (Fig. 7).

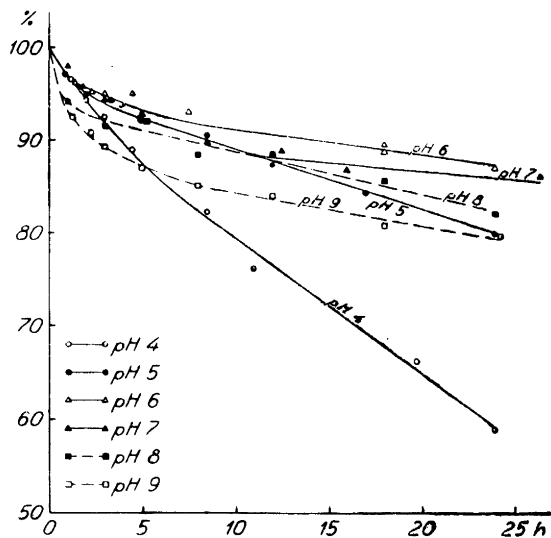


Fig. 5. The yield of sulphite treated wood as a function of the heating time at 135° for sulphite solutions of different pH.

Because of the formation of sulphonic acid groups, the pH of the solutions decreases during the heating periods, the change being greatest for solutions whose pH initial was 4, 5, and 9 because of the low buffer capacity of sulphite solutions at these pHs. At pH 4 it decreased after 24 hours to 3.3; at pH 5, to 4.3; at pH 6, to 5.8; at pH 7, to 6.7; at pH 8, to 7.9; and at pH 9, to 8.5.

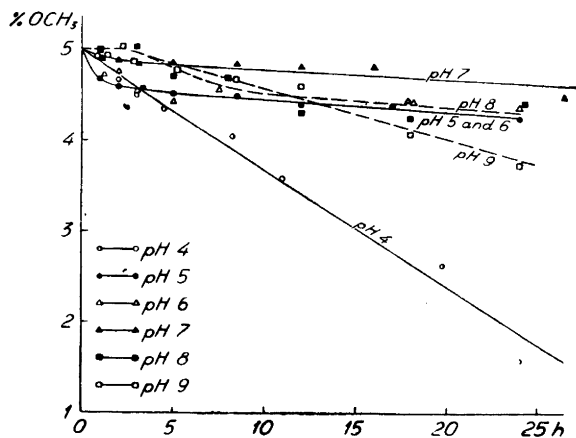


Fig. 6. The methoxyl content of the sulphite treated wood as a function of the heating time at 135° for sulphite solutions of different pH.

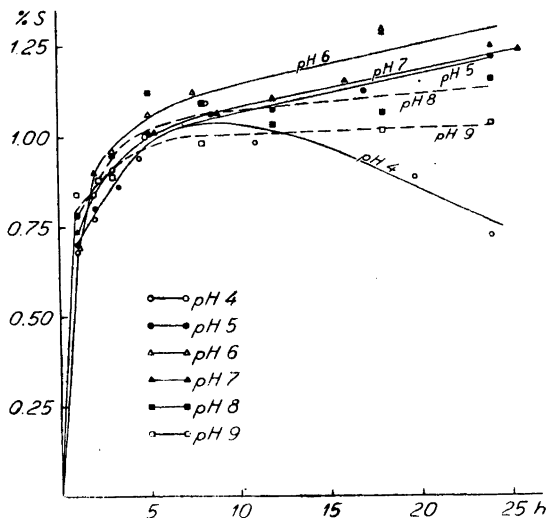


Fig. 7. The sulphur content of the sulphite treated wood as a function of the heating time at 135° for sulphite solutions of different pH.

### Spectrophotometric determination of dissolved lignin-sulphonic acid

Wood powder (10 g) was treated with sulphite solution (300 ml, pH 4.9–8.0) as described above, for 4 hours at 135°. The powder was filtered off and washed with sufficient water to give a total volume of 1 000 ml. The resulting solutions were then diluted 10 times. The ultra-violet absorption of these solutions was determined using a Beckman spectrophotometer and the content of lignin-bound methoxyl in the solutions was calculated assuming that  $\log \epsilon = 3.5^{18}$  (concentration measured in equivalents of methoxyl per litre) for a ligninsulphonic acid at the absorption maximum at 280  $m\mu$ . In Table 2 is given the number of dissolved lignin-bound methoxyl groups as a percentage of the number of lignin-bound methoxyl groups in the original wood powder. Fig. 3 shows the ultra-violet absorption curves of the different solutions.

### Alkali treatment of the sulphonated wood powders

Sulphonated wood powder (1.5 g of the preparations which had been sulphonated for 2 and 24 hours) was treated with a NaOH solution (25 ml, 5 g NaOH per litre). The mixture was allowed to stand 4 hours at room temperature, then the powder was collected and washed with water. The yield of wood powder was quantitative. The methoxyl content was determined on one sample: very little (about 4 %) of the methoxyl groups in the sulphonated wood had been dissolved by the alkali treatment. For powders which had been treated with sulphite solutions of pH 7 or less, the sulphur contents decreased 0.11–0.17 % (absolute). For pHs greater than 7, the decreases were 0.01–0.04 %.

Treatment of the sulphonated wood powders with fuming hydrochloric acid by Richtzenhain's method<sup>6</sup>

Sulphonated wood powder (5 g of the preparations which had been sulphonated for 1 hour) was allowed to stand with fuming hydrochloric acid (saturated at  $-6^{\circ}$ ) at  $-4^{\circ}$  for 24 hours with occasional shaking. The insoluble product was filtered off and washed with concentrated hydrochloric acid (s. g. 1.18) until the filtrate was colourless and did not give any turbidity when diluted with water, then washed with water, and with saturated sodium bicarbonate solution, and finally again with water. The preparation was analysed for sulphur and methoxyl. The results are given in Table 1.

SUMMARY

1. Extracted wood powder (spruce, *Picea abies*) had been treated at  $135^{\circ}$  with sulphite solutions, for times varying from 1 to 24 hours, and at pHs varying from 4 to 9.

2. Only a small fraction of the lignin is dissolved at pH 6—7. This part seems to be bound by weaker linkages than the remainder.

3. The dissolution of the bulk of the lignin with sulphite solutions of different pH closely parallels the hydrolysis of the dibenzyl ether linkage of diveratryl ether.

4. The lignin which is not dissolved, is sulphonated very rapidly to a sulphur content of 0.18—0.22 sulphur atom per methoxyl group. A slower sulphonation then follows. After 24 hours the wood contains 0.25—0.28 sulphur atom per methoxyl group.

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