

Studies on Lignin

VI*. Nitrobenzene Oxidation of Lignin Sulphonic Acids

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Lignin sulphonic acids from sulphite waste liquors are of considerable interest as raw material for the manufacture of vanillin, and many papers dealing with this subject have been published¹. Of the numerous oxidation procedures suggested, the method employing nitrobenzene and alkali seems to be one of the most promising because of the high yields obtainable.

Little has been done, however, to correlate these yields with the method of preparation, sulphur content, pretreatment *etc.* of the sulphonic acids employed. In their original paper², Freudenberg, Lautsch and Engler stated that the yield of vanillin from lignin in ordinary sulphite waste liquor was 10–20 % lower than that obtainable directly from the lignin in the wood. Later, Lautsch and Piazzolo³ isolated several fractions of lignin sulphonic acids from sulphite waste liquor by fractional precipitation with benzacridine and showed that these fractions gave yields which varied from 15 to 27 % (on the basis of the weight of lignin), the yield increasing with the sulphur content.

During the course of a normal sulphite cook, however, the lignin is subjected to rather drastic treatment, and some of the results previously obtained may be due to the occurrence of secondary reactions during this process, thus making it difficult to draw any definite conclusions about the influence of different variables on the yield of vanillin.

In the present paper, therefore, so-called "low sulphonated lignin"⁴ has been employed for a study of the nitrobenzene oxidation of lignin sulphonic acids, since this material is prepared under very mild conditions.

The "low sulphonated lignin" was heated with sulphite solutions of various pH, for different lengths of time, and the products were analyzed and sub-

* Part V. *Svensk Kem. Tid.* 63 (1951) 195.

jected to oxidation with nitrobenzene and alkali. The results are shown in Table 1 and Fig. 1.

The analytical values for sulphur, barium, and methoxyl are based on the weight of dry material, while the yields of sulphonation products and vanillin are based on the amount of methoxyl recovered. The sulphite solutions (75 ml for 4 g of material) all contained 6 % of total sulphur dioxide and sufficient sodium hydroxide to give the desired pH. The reaction temperature was 135°.

Table 1. Sulphonation of "low sulphonated lignin".

pH of sulphite soln. *	Time h	Yield %	Content of			2Ba/S	Yield of vanillin %
			sulphur %	barium %	methoxyl %		
—	—	—	4.3	9.8	12.0	1.06	31.9
1.4	2	71	5.6	12.3	11.7	1.03	—
1.4	6	74	6.9	14.9	10.7	1.01	—
1.4	12	77	7.9	17.9	9.5	1.06	32.1
1.4	24	70	8.0	18.6	9.0	1.08	31.6
3.4	4	76	4.7	10.6	11.9	1.04	—
3.4	10	72	5.2	11.3	11.8	1.02	—
3.4	24	68	6.4	14.5	11.0	1.06	—
3.4	48	76	7.7	17.3	10.6	1.05	31.2
5.8	8	70	4.7	11.1	12.1	1.09	—
5.8	24	70	5.2	11.5	11.8	1.03	31.6
5.8	72	75	6.4	15.8	10.2	1.14	32.3

* Measured at room temperature. The initial and final pH's of the solutions were the same.

Fig. 1 shows the ratios S/OCH₃ for different pH values as functions of the time of heating.

In strongly acid solutions the uptake of sulphur is rather rapid, in agreement with the findings of Erdtman⁴, and Erdtman, Hägglund and Lindgren⁵ who showed further that this is not so for lignin sulphonic acids from an ordinary acid sulphite waste liquor, which are sulphonated only to a small extent. The rate of sulphonation decreases with time and the ratio S/OCH₃ finally approaches unity.

At higher pH values, sulphonation takes place to an appreciable extent, although at a much lower rate. However, the rate seems to decrease only

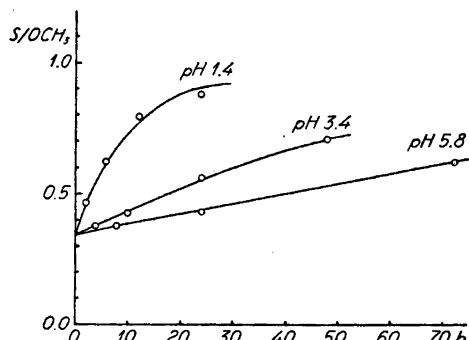


Fig. 1. Sulphonation of "low sulphonated lignin" at different pH-values.

slowly with time and this indicates that most of the reactive groups in "low sulphonated lignin" can be sulphonated in almost neutral media. In the wood, on the other hand, lignin cannot be sulphonated to more than 0.33 sulphur atom per methoxyl group at pH 6, even on prolonged heating⁶. On dissolution of the lignin sulphonic acids from the sulphonated wood, the unsulphonated groups (Group B⁷) are apparently converted into groups showing an increased reactivity towards sulphite, probably by hydrolytic fission of an acetal⁸ or benzyl ether^{9,10} linkage with formation of a reactive hydroxyl group¹¹ (Group B'⁸).

The yield of vanillin is completely independent of the degree of sulphonation, in agreement with previous model experiments¹². The average yield of vanillin, 31.8 %, is somewhat higher than that obtained from spruce wood directly (for the wood employed here, 30.5 %). However, the latter yield is based on the methoxyl content of the wood, and probably almost 10 % of the methoxyl groups originate from non-lignin material¹³. When allowance is made for this, the vanillin yield from the wood becomes about 33.5 %, somewhat higher than the figure for "low sulphonated lignin". The latter represents only part of the total lignin in the wood, however, and it will be shown in a later communication that the β -lignin sulphonic acids contain fractions which give vanillin in yields of almost 40 %. It is therefore justifiable to say that sulphonation in itself does not change the yield of vanillin at any stage.

It is well known that when lignin sulphonic acids are heated with alkali, some vanillin is obtained, the amount generally being 4–7 % of the weight of the lignin^{14–16}. We have now studied the effect of alkaline pretreatment of "low sulphonated lignin" on the yield of vanillin obtained on oxidation with nitrobenzene and alkali. The heating with alkali was carried out both in the presence and absence of sulphite (*cf.* experimental part) at a temperature of 135° for various lengths of time. The pH employed was 11.4 (measured at

Table 2. Alkaline treatment of "low sulphonated lignin" and subsequent nitrobenzene oxidation.

Time hours	Sulphite present	Yield %	Content of			2Ba/S	S/OCH ₃	Yield of vanillin %	
			sulphur %	barium %	methoxyl %			During alkali treatment	On subsequent nitrobenzene oxidation
0	—	—	4.3	9.8	12.0	1.06	0.34	—	31.9
2	+	63	4.7	11.3	11.5	1.11	0.40	—	31.3
6	+	52	5.3	13.6	10.9	1.18	0.48	—	28.0
12	+	41	6.3	14.8	10.6	1.21	0.55	4.2	27.0
2	—	63	4.0	9.4	12.0	1.09	0.32	—	31.1
6	—	50	3.6	9.2	12.5	1.18	0.28	—	28.8
12	—	40	3.0	7.5	12.9	1.20	0.23	3.9	27.0

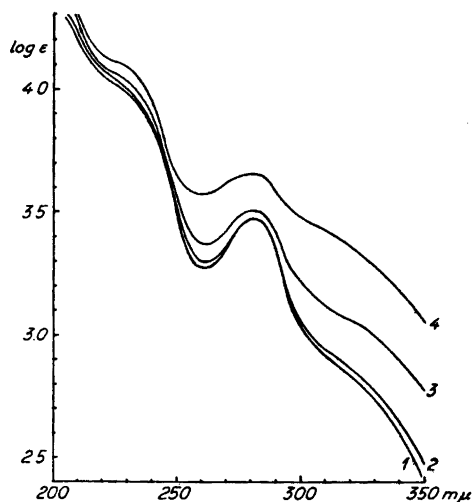
room temperature). The results obtained are listed in Table 2. (Analytical figures calculated as in Table 1.)

It is evident that the decrease in the yield of vanillin obtained after oxidation corresponds approximately to the amount of vanillin obtained on alkaline hydrolysis of the lignin sulphonic acids, and thus the total amount of vanillin obtained from the lignin remains constant.

However, serious changes do occur during the alkaline treatment. Thus, unlike untreated "low sulphonated lignin", the products obtained give barium salts which are soluble in ethanol and precipitate only on the addition of ether. The material is dark grey in colour, and gives solutions which are almost black. The barium/sulphur ratios increase with time of heating, indicating the formation of carboxyl groups. Further, the yields of products decrease with time of heating to rather low values, and, finally the ultra-violet spectra become progressively distorted with flattening of the maxima and increased absorption in the 300–350 m μ region. This is not the case when the sulphonation is carried out in neutral or acid media¹⁷ (Fig. 2).

When lignin is heated with acids, particularly in the presence of reactive phenols, the reactivity towards sulphite is greatly reduced^{7,18}. This effect is believed to involve the condensation of reactive groups, at least partly of benzyl alcoholic character. As a result of this condensation, the α -carbon atoms of some of the elements would become attached to two aromatic nuclei.

Fig. 2. Ultra-violet absorption curves of
 (1) "low sulphonated lignin"
 (2) "low sulphonated lignin" sulphonated at pH 5.8 for 72 hours
 (3) "low sulphonated lignin" sulphonated at pH 11.4 for 6 hours
 (4) "low sulphonated lignin" sulphonated at pH 11.4 for 12 hours



The ϵ -values are based on the equivalent weights, calculated from the methoxyl content.

This would make them incapable of yielding vanillin¹⁹, and thus the yield of vanillin would be reduced. To study this effect, lignin sulphonic acids of different degrees of sulphonation (obtained by sulphonation of "low sulphonated lignin") were subjected to heating with sulphuric acid solutions of pH 1.4 and pH 0.5, respectively, in the presence of resorcinol (1 g/g of lignin

Table 3. Treatment of "low sulphonated lignin" with resorcinol in acid solution, and subsequent nitrobenzene oxidation.

Time hours	Yield %		S/OCH ₃		Yield of vanillin %	
	pH 0.5	pH 1.4	pH 0.5	pH 1.4	pH 0.5	pH 1.4
0	—	—	0.34	0.34	31.9	31.9
2	60	65	—	0.35	16.5	22.0
6	60	62	—	—	12.7	17.5
12	62	57	0.35	0.34	13.5	17.1
0	—	—	0.49	0.49	32.3	32.3
2	69	66	—	—	—	23.9
6	68	60	—	—	19.5	24.6
12	62	64	0.45	0.51	18.6	24.1
0	—	—	—	0.62	—	31.6
6	—	70	—	—	—	27.0
12	—	68	—	0.60	—	26.3

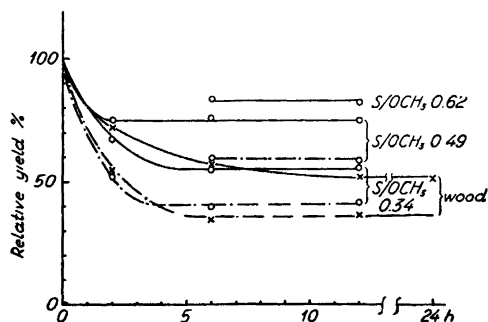


Fig. 3. Relative yields of vanillin from lignin sulphonic acids of different degrees of sulphonation and from wood, previously heated with resorcinol in sulphuric acid solutions of pH 0.5 (---) and pH 1.4 (—).

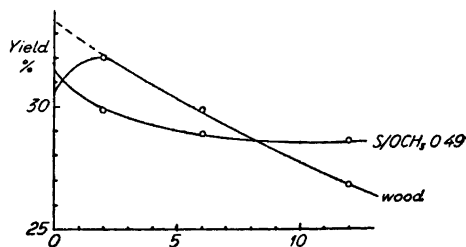


Fig. 4. Yields of vanillin from a lignin sulphonic acid and from wood, previously heated with sulphuric acid.

sulphonic acid), and subsequently oxidized with nitrobenzene and alkali. The temperature employed in the acid treatment was 135°. The results obtained are given in Table 3 and Fig. 3.

In Fig. 3, the yields of vanillin from the different preparations described in Table 3, (expressed as per cent of the yield obtained from untreated "low sulphonated lignin") are plotted against the time of heating with resorcinol and acid. For comparison, the corresponding yields from extracted spruce, heated under the same conditions, are given.

Fig. 4 shows the yields of vanillin for wood and for a lignin sulphonic acid (See Table 3, S/OCH₃ = 0.49), heated with a sulphuric acid solution of pH 1.4, without the addition of resorcinol.

Fig. 3 shows that the condensation responsible for the decrease in the yield of vanillin is a fairly rapid reaction, and that only some of the vanillin-yielding elements in the lignin sulphonic acids contain reactive groups available for condensation. The number of such available groups decreases with increasing degree of sulphonation, the reactive groups being blocked by sulphonic acid residues^{7,18}. The experiments with wood show, however, that part of the vanillin-yielding elements of the lignin contain groups which are "blocked" even in the wood. Some of these groups (ca. 0.15 per methoxyl group) remain unaffected at pH 1.4 but react with resorcinol at pH 0.5. The same effect is exhibited by the lignin sulphonic acids, and in this case also the proportion of groups behaving in this way is ca. 0.15 per methoxyl group.

It is further seen that the introduction of sulphonic acid groups to form "low sulphonated lignin" (sulphonation of group A⁷) has very little influence

on the decrease in the yield of vanillin caused by the condensation of the lignin with resorcinol. Thus, the major part of group A probably belongs to elements which are not originally capable of yielding vanillin, *i. e.* "condensed elements"¹² or, possibly elements of the pinoresinol type¹³. On further introduction of sulphonic acid groups (sulphonation of group B), the effect on the vanillin yield is considerable, although decreasing in the later stages of the sulphonation. Thus group B probably belongs largely to elements of the open type¹², of which at least 25 % are rather stable towards acids and reactive phenols.

Fig. 4 shows that even in the case of treatment with acids in the absence of added phenol, sulphonation renders the lignin more stable toward condensing reagents, although the effect is less pronounced, because of the lower rate of condensation.

The maximum in the curve for acid-treated wood (in Fig. 4) may be caused by a rapid dissolution of non-lignin methoxyl-containing components present in the wood¹³, thus causing an apparent increase in the yield of vanillin based on the methoxyl content. The dashed line indicates the yield of vanillin based on methoxyl, corrected for this "extra" methoxyl.

EXPERIMENTAL

The "low sulphonated lignin" was prepared essentially as described by Erdtman⁴. The further sulphonation of this material was carried out as follows:

A solution of "low sulphonated lignin" (barium salt) was passed through a column of Amberlite IR 120. The effluent was neutralized with sodium hydroxide, and sulphur dioxide corresponding to 6 % of the final amount of solution was absorbed. The solution was then divided into samples, each containing 4 g of the lignin sulphonic acid salt. Sodium hydroxide was added to the samples until the desired pH was reached, and the volumes were adjusted to 75 ml.

After heating in an autoclave of stainless steel at 135° for a predetermined length of time, each sample was cooled and freed from excess sulphur dioxide by a stream of carbon dioxide. The sodium ions were exchanged for hydrogen ions, and the solution was neutralized with barium carbonate, filtered, evaporated *in vacuo* to ca. 35 ml, and centrifuged. The clear solution was then poured, with vigorous stirring, into absolute ethanol (150 ml) containing, if necessary, ether (50 ml). The precipitate was separated by centrifugation and then washed twice with ethanol and three times with ether. The product was obtained as a fine powder of very light cream colour (except in the case of alkaline sulphonation).

The acid and alkaline treatments were carried out in essentially the same way. The acid solutions were prepared by adding dilute sulphuric acid to a solution, containing the sulphonic acid and 1.4 % of sodium hydroxide, until the desired pH was reached. Samples corresponding to 4 g of sulphonic acid were diluted to 75 ml, and resorcinol (4 g) added if desired. The alkaline solutions containing no sulphite were prepared in the same way as the corresponding sulphite solutions, but instead of sulphur dioxide, sulphuric acid was added until a pH of 11.4 was reached.

The products obtained on heating with resorcinol were of a red colour and rather soluble in ethanol, while those obtained on heating with acid were brownish and, in some cases, difficultly soluble in water.

— In the experiments with wood, 5 g samples of extracted spruce wood flour (*Picea abies* (L.) Karst.) were heated with 40 ml each of the acid solution described above. The amount of resorcinol employed was 0.3 g/g of wood.

— The undissolved residues were filtered off, washed thoroughly with water and acetone and dried at 105° for 4 hours.

The analyses were carried out on samples dried *in vacuo* over phosphorous pentoxide and paraffin at 70° for about one week. Sulphur was determined by a modified Grote-Krekeler²⁰ method and methoxyl by the Vieböck-Schwappach²¹ method. The nitrobenzene oxidations and vanillin determinations were carried out as described previously^{12, 22}. The UV-spectra were determined with a Beckman spectrophotometer, model DU.

SUMMARY

“Low sulphonated lignin” has been heated with sulphite solutions of various pH, and with alkali, for different lengths of time. It has also been heated in acid solution either alone or in the presence of resorcinol. The products obtained were analyzed and oxidized by means of nitrobenzene and alkali.

The following conclusions may be drawn from the results:

The major part of the reactive groups in “low sulphonated lignin” (Group B) may be sulphonated in almost neutral media, although at a low rate.

The yield of vanillin obtained on oxidation with nitrobenzene and alkali is not affected by sulphonation.

Alkaline treatment of “low sulphonated lignin” causes deep-seated changes in the structure, even in the presence of sulphite, but the total yield of vanillin seems to be relatively constant.

Sulphonation renders the lignin more stable toward condensing agents, sulphonic acid residues blocking reactive groups.

The major part of the sulphonated groups in “low sulphonated lignin” (Group A) probably belong to “condensed elements”, or, possibly elements of the pinosresinol type, while the remainder of the groups (Group B) belong largely to elements of the open type, of which at least 25 % are rather stable toward acids and reactive phenols.

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