# Studies on Lignin

VII *. β-Lignin Sulphonic Acids

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While the preparation of so-called α-lignin sulphonic acids is comparatively simple, the isolation of the low molecular weight β-lignin sulphonic acids in a "pure" state offers considerable difficulties [1-3], since they are accompanied by carbohydrate material of acidic character which is very difficult to remove. Consequently, the β-fractions have not been so extensively studied as the α-fractions. However, the chemistry of the low molecular lignin fractions is a matter of great interest, and renewed attempts have now been made to find methods for the isolation of β-lignin sulphonic acids in the purest possible condition without excessive loss.

Erdtman [4-6] studied the step-wise precipitation of lignin sulphonic acids from waste liquors by means of various amines and found that compounds of the general structure

$$R - NH - CO - CH \overset{\displaystyle R_2}{\underset{\displaystyle R_1}{\overset{|}{-}} N} \diagdown R_3$$
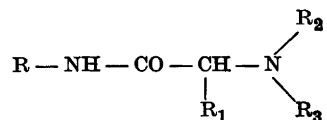
showed considerable promise and that 1-(N-piperidinoacetylamino)-naphthalene ("PAN", $C_{10}H_7-NH-CO-CH_2-NC_5H_{10}$) is a powerful precipitating agent. This compound and two new analogues derived from anthraquinone, 1-(N-piperidinoacetylamino)-anthraquinone ("PAA") and 1,5-bis(N-piperidinoacetylamino)-anthraquinone ("BPA"), together with S-1-naphthylmethylthiuronium chloride [7] ("NMT") have now been employed for precipitation experiments. For comparison, bis-(4-dimethylaminophenyl)-

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methane ("BIS") was studied, since this reagent is generally considered to leave the β-lignin sulphonic acids in solution [5].

The experiments were carried out with "liquors" obtained by heating spruce wood flour with a sulphite solution of pH 5.3 at 135° for about 15 hours [8] (*cf.* experimental part). Under these conditions, ca. 30 % of the lignin in the wood dissolves and, since the lignin sulphonic acids are formed under very mild conditions, they provide excellent material for the study of the β-fraction.

Two different liquors, one freshly prepared (A) and one about a year old (B) were employed. Liquor B was also precipitated after concentration to about one third of its original volume. All the precipitating agents, except "NMT", were used in the form of their sulphates in aqueous solution.

The methoxyl content of the liquor after precipitation was determined, and thus the percentage of lignin sulphonic acids precipitated estimated roughly. The results obtained are listed in Table 1.

Table 1. Methoxyl precipitated with different reagents.

Reagent	Methoxyl precipitated %		
	A	B directly	B conc.
BIS	22	27	28
BPA	67	65	70
NMT	63	68	—
PAN	80	73	79
PAA	86	84	87

It is evident from the table that the age and concentration of the liquor has only a small influence on the values.

Only about 25 % of the lignin sulphonic acids are precipitated with BIS, the remainder being of rather low molecular weight.

PAA is clearly the most powerful precipitant of the reagents studied, and furthermore, as it is strongly coloured (yellow) it is easier to ensure that the final product is free from precipitating agent. Consequently, PAA was employed for the isolation of a large amount of lignin sulphonic acids from the liquor A. The product obtained was then divided into three fractions by consecutive precipitations with BIS (fraction a_1), BPA (fraction a_2), and PAA (fraction a_3). In a separate experiment, a lignin sulphonic acid preparation (fraction b) was isolated by means of NMT from liquor B, previously precipitated with BIS.

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The sulphonic acids were converted into barium salts and these preparations were analyzed and oxidized with nitrobenzene and alkali.

The results are listed in Table 2, where the yields of vanillin are based on the methoxyl content of the lignin sulphonic acids, while the yields of products are calculated as methoxyl recovered as a percentage of the total methoxyl in the liquor. For comparison, the yields of the different fractions, calculated from Table 1, are given.
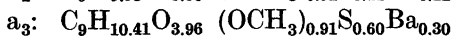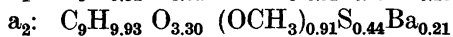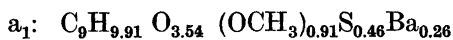
Table 2. Composition of lignin sulphonic acid fractions.

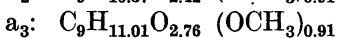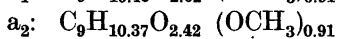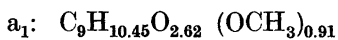| Fraction | Yield % | | Analyses | | | | | | | 2Ba/S | S/OCH$_3$ | Yield of vanillin % |
	Found	Calc.	S %	Ba %	OCH$_3$ %	C %	H %	Cu$_I$*	Cu$_{II}$**			
a$_1$	15	22	5.8	13.9	11.2	47.1	5.0	7.1	34.1	1.13	0.50	33.0
a$_2$	31	45	5.8	12.3	11.6	49.0	5.3	2.9	10.6	0.99	0.48	36.0
a$_3$	14	19	7.2	15.4	10.4	43.9	4.9	0	7.1	1.00	0.66	38.3
b	26	41	6.1	14.0	10.3	—	—	2.2	5.0	1.07	0.57	36.8

* Copper number prior to hydrolysis.
** Copper number after hydrolysis.

The amount of methoxyl recovered is quite low compared with the figures in Table 1, due to losses in different stages of the preparation. The "purity" of the fractions a$_2$ and a$_3$, which may be considered as β-lignin sulphonic acids, is very high, as judged by their low reducing power and their barium/sulphur ratio.

From the analyses in Table 2, the following empirical formulae are derived.

a$_1$: $C_9H_{9.91}O_{3.54}(OCH_3)_{0.91}S_{0.46}Ba_{0.26}$
a$_2$: $C_9H_{9.93}O_{3.30}(OCH_3)_{0.91}S_{0.44}Ba_{0.21}$
a$_3$: $C_9H_{10.41}O_{3.96}(OCH_3)_{0.91}S_{0.60}Ba_{0.30}$

The following formulae are obtained on a sulphur- and barium-free basis, by substituting $SO_3\dfrac{Ba}{2}$ for OH:

a$_1$: $C_9H_{10.45}O_{2.62}(OCH_3)_{0.91}$
a$_2$: $C_9H_{10.37}O_{2.42}(OCH_3)_{0.91}$
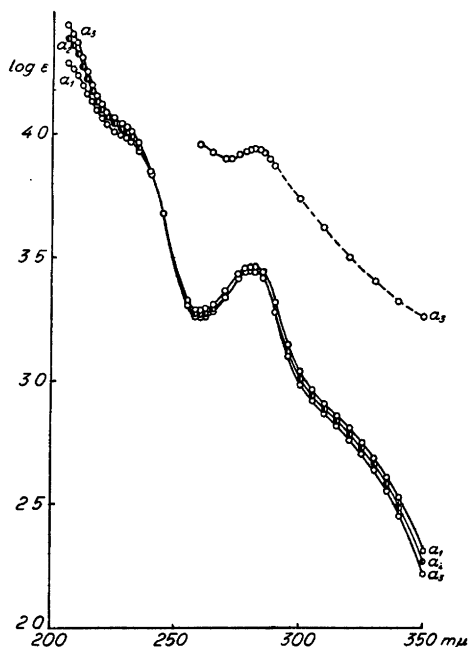a$_3$: $C_9H_{11.01}O_{2.76}(OCH_3)_{0.91}$

Fig. 1. Ultra-violet absorption spectra of fractions a_1, a_2, and a_3 in water (————) and of fraction a_3 in 0.1 N NaOH (— — — —). The ordinates of the latter curve have been increased by 0.5. The ε-values are based on the equivalent weight, calculated from the methoxyl content.
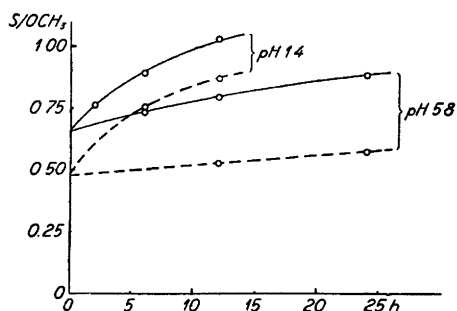
Fig. 2. Sulphonation of fractions a_2 (— — — —) and a_3 (————) at pH 1.4 and 5.8.

When these formulae are compared to those given by Erdtman, Lindgren, and Pettersson [9] for "low sulphonated lignin", the only significant difference is the appreciably higher hydrogen content of the β-lignin sulphonic acids. As the oxygen content is "normal", this cannot imply that the two types of material differ only by the addition or removal of water. The methoxyl content is only slightly lower than the average of the recorded values for α-lignin sulphonic acids and the very low methoxyl values found previously for β-fractions [1] must be ascribed to contamination with carbohydrate material.

The ultra-violet absorption spectra of fractions a_1, a_2, and a_3 are shown in Fig. 1.

No appreciable differences seem to exist between the different fractions, and the curves are very similar to those of "low sulphonated lignin".

The most interesting figures in Table 2 relate to the yields of vanillin, which increase with decreasing molecular weight to values almost 20 % higher than the average value for spruce lignin. Thus, low molecular lignin probably contains fewer "condensed elements" [10], i.e. elements which are connected by carbon-carbon linkages.

Examination of the aldehydic oxidation products, by means of paper chromatography, as described in Part III [11], revealed that, in addition to vanillin, p-hydroxybenzaldehyde, syringaldehyde and 5-formylvanillin were present in approximately the same amounts as are obtained by direct oxidation of the wood. This also applies to "low sulphonated lignin" (cf. Part VI). In this connection it may be mentioned that the aldehydic mixture obtained on "anaerobic" alkaline hydrolysis of lignin sulphonic acids * contained p-hydroxybenzaldehyde in addition to vanillin, but no trace of syringaldehyde or 5-formylvanillin.

To estimate the content of phenolic hydroxyl groups in the β-lignin sulphonic acids, the ultra-violet absorption spectrum of fraction a_3 in 0.1 N sodium hydroxide solution was determined. (Dashed line in Fig. 1.) The displacement of the 280 mμ maximum is very small (ca. 2 mμ), indicating a

Table 3. Sulphonation of β-lignin sulphonic acids.

Fraction	pH	Time hours	Yield %	Analyses					2Ba/S	Yield of vanillin %
				S %	Ba %	OCH$_3$ %	Cu$_I$	Cu$_{II}$		
a_2	1.4	6	68	7.5	16.3	9.4	—	—	1.01	31.3
»	1.4	12	65	7.8	17.6	8.7	0	1.0	1.05	30.1
»	5.8	12	72	6.3	13.4	11.5	—	—	0.99	—
»	5.8	24	68	6.8	13.9	11.4	0	2.8	0.96	36.4
a_3	1.4	2	65	7.5	16.8	9.6	—	—	1.04	—
»	1.4	6	66	7.9	18.1	8.7	—	—	1.07	34.2
»	1.4	12	70	9.1	20.5	8.5	0	0	1.04	33.5
»	5.8	6	71	7.4	16.7	9.8	—	—	1.05	—
»	5.8	12	64	7.7	17.3	9.4	—	—	1.04	37.6
»	5.8	24	67	8.0	17.8	8.7	0	3.9	1.04	38.5

* Kindly supplied by Dr. E. Adler.

phenolic hydroxyl content of the same order of magnitude as in "low sulphonated lignin"[12].

In Table 3 the results of sulphonating fractions a_2 and a_3 at pH 1.4 and 5.8 are shown, the yields of products and of vanillin being 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, and the reaction temperature used was 135°.

Fig. 2 shows the S/OCH_3 ratio as function of the time of heating for different pH-values.

The results show that fractions a_2 and a_3 are sulphonated at about the same rate as "low sulphonated lignin" at pH 1.4 (cf. Part VI), but fraction a_3 (the fraction of lowest molecular weight) may be sulphonated to S/OCH_3 ratios exceeding unity. Further, at pH 5.8, fraction a_3 is sulphonated much faster than "low sulphonated lignin" or fraction a_2, which sulphonate at exactly the same rate. Thus fraction a_3 differs from the bulk of the lignin, not only in the content of groups reactive towards sulphite, but also in the character of those groups.

When β-lignin sulphonic acids are heated with a sulphite solution of pH 1.4, the yield of vanillin subsequently obtained decreases rather rapidly initially and appears to reach a constant value. This phenomenon is not exhibited by "low sulphonated lignin", does not take place if the sulphite solution has pH 5.8, and appears to involve 15—20% of the vanillin-yielding elements initially present. This percentage agrees well with the amount of "extra" vanillin obtained from the β-sulphonic acids and it seems reasonable to assume that acid-sensitive groups are the ones responsible for this "extra" vanillin. This may be thought to imply that the bulk of the lignin contains such acid-sensitive groups, but that these are destroyed in the preparation of "low sulphonated lignin". This is, however, unlikely as the only acid treatment in the preparation of the latter involves heating at pH about 2 at a temperature of 80—90° for three hours; that is to say much milder acid treatment than was employed in the sulphonation of the β-lignin sulphonic acids. Furthermore, the yield of vanillin obtained directly from the lignin in the wood only exceeds that obtained from "low sulphonated lignin" by a small amount, just enough to cover the "extra" amount formed from the lowest molecular weight portion (cf. Part VI).

EXPERIMENTAL

1- (N-Piperidinoacetylamino)-naphthalene. 1-Chloroacetylamino-naphthalene [13] (35 g) was suspended in dry toluene (300 ml) and piperidine (36 ml) added portionwise. The temperature soon rose, all the material dissolved, and when almost all the piperidine had been added, piperidine hydrochloride commenced to separate. When the reaction

was over, the mixture was cooled and filtered, and the solid material washed with toluene. The filtrate and washings were extracted with dilute sulphuric acid, and the acid solution was made alkaline with sodium hydroxide. The colourless material (36.8 g, 86%) which precipitated was collected by filtration, washed and dried and after two recrystallizations from ethanol formed colourless plates, m.p. 116—116.5°.

$C_{17}H_{20}ON_2$ Calc.   N 10.4   Equivalent weight 268.4
                  Found » 10.5   »   »   267.2

1-(N-Piperidinoacetylamino)-antraquinone.   A mixture of 1-chloroacetylamino-antraquinone [14] (30 g), piperidine (50 ml) and dry xylene (500 ml) was refluxed for one hour, then cooled and extracted with dilute sulphuric acid. The dark red acid solution was made alkaline with sodium hydroxide, and the yellowish-green precipitate formed (34.5 g, 99%) was collected by filtration, washed with water, dried and repeatedly recrystallized from dioxan, giving yellow needles, m.p. 240—242° (decomp.).

$C_{21}H_{20}O_3N_2$ Calc.   N 8.0   Equivalent weight 348.4
                  Found » 7.7   »   »   350.4

1,5-Bis-(chloroacetylamino)-antraquinone.   A mixture of 1,5-diaminoantraquinone [15] (40 g) and chloroacetyl chloride (52 g) in nitrobenzene (400 ml) was heated at 130° until hydrogen chloride ceased to be evolved (ca. 15 minutes). The dark green material (53 g, 81 %) which separated from the solution on cooling was collected by filtration and washed with nitrobenzene and ether and dried. Recrystallization from nitrobenzene gave dark green plates which decomposed at 315°.

$C_{18}H_{12}O_4N_2Cl_2$ Calc.   Cl 18.2   N 7.2
                  Found » 17.8   » 7.2

1,5-Bis-(N-piperidinoacetylamino)-antraquinone.   A mixture of the above material (30 g), piperidine (75 ml) and dry xylene (500 ml) was refluxed for one hour, then cooled and extracted with dilute sulphuric acid. The brownish-red acid solution was made alkaline with sodium hydroxide and the red precipitate (36.5 g, 97 %) collected by filtration, washed with water and dried. Repeated recrystallization from dioxan yielded orange needles, m.p. 261—262° (decomp.).

$C_{28}H_{32}O_4N_4$ Calc.   N 11.5   Equivalent weight 244.3
                  Found » 11.0   »   »   241.9

Precipitation experiments

Two different liquors (A and B) were employed. Liquor A was freshly prepared from extracted spruce wood flour (*Picea abies* (L) Karst.) (corresponding to 1.68 kg dry weight) and a solution of pH 5.3 (8.4 l) containing crystallized sodium sulphite (335 g) and sodium pyrosulphite (845 g). The mixture was heated in an electrically-heated rotating autoclave to 130° in the course of 4 hours, then to 135° in a further 2 hours and maintained at that temperature for 14 hours. The autoclave was kept rotating until it was cool, then the contents were filtered. The solid was washed with lukewarm water and the washings

combined with the filtrate which was brownish yellow in colour and had pH 5.25. The total volume was 11.5 litres, the content of solids was 130 g/l and the methoxyl content of the solids 1.87 %.

Liquor B had been prepared about one year previously, in essentially the same way as A. The content of solids was 133 g/l and the methoxyl content of the solids 1.94 %.

The precipitating power of the different reagents was determined in the following way:

To the liquor to be precipitated (100 ml) was added an excess of the reagent dissolved in the equivalent amount of dilute sulphuric acid (in the case of naphthylmethylthiuronium chloride (NMT) dissolved in hot water). The mixture was stirred vigorously and the volume adjusted to 150 ml. The pH after precipitation varied between 4.5 and 5.3. The mixture was set aside overnight, then the precipitate was collected by centrifugation and washed thoroughly with water. The mother liquor and washings were combined, the volume adjusted to 250 ml, and aliquots taken for the determination of the methoxyl and solid contents.

In the methoxyl determinations [16], an extra absorption vessel containing cadmium sulphate solution [17] (to remove hydrogen sulphide) was used in order to avoid the difficulties encountered by Abrahamsson, Lindgren and Hägglund [3]. It was later found, however, that no extra precautions were necessary if the amount of bromine in the absorption vessel was large compared with the amount of sulphate and sulphite in the sample, at least if the gas was washed with bicarbonate solution before absorption in the bromine reagent.

After determining the minimum amount of the reagents BIS, PAA and BPA necessary for complete precipitation of liquor A, a larger amount of lignin sulphonic acid was isolated.

PAA (125 g), dissolved in the equivalent amount of dilute sulphuric acid was added to liquor A (5.6 l). The mixture was set aside overnight, then the supernatant liquid was decanted and the precipitate was squeezed to remove adhering solution as completely as possible. The solid was then converted portionwise to sodium salt by treatment with 1 % sodium hydroxide in a mortar, care being taken to avoid excess of alkali and to keep pH as close to 7 as possible. The mixture was centrifuged and the precipitate washed with water.

The combined solutions (1 l), containing the sodium salts of the precipitated lignin sulphonic acids, were then fractionated as follows:

BIS (35 g), dissolved in sulphuric acid, was added. The precipitate obtained was separated and washed and the sulphonic acids recovered as the sodium salts as described above, then converted to the barium salts (fraction a_1) by means of an ion-exchanger as described in Part VI. The original mother liquor was made slightly alkaline (pH 10) and the excess of BIS was centrifuged off. The solution was neutralized and a solution of BPA (55 g) in dilute sulphuric acid was added. The precipitate was converted into the barium salt as described above (fraction a_2) and the original solution was treated with PAA (45 g), dissolved in sulphuric acid. Conversion of the precipitate into the barium salt gave fraction a_3.

In a similar way liquor B was first precipitated with BIS and then with NMT. The product obtained from the latter was purified by reprecipitation with NMT (fraction b).

Fractions a_2 and a_3 were further sulphonated by the method described in Part VI.

The oxidations with nitrobenzene and alkali and the vanillin determinations were carried out as described previously [10], [11].

SUMMARY

A method for the isolation of so-called β-lignin sulphonic acids in a "pure" state by precipitation with basic reagents has been devised.

The products, which were isolated from a solution obtained by heating wood with a sulphite solution of pH 5.3, had a higher sulphur content than "low sulphonated lignin". The yields of vanillin from the β-lignin sulphonic acids were higher than for the average lignin, and increased with decreasing molecular weight.

Further sulphonation of the β-acids showed, that at low pH-values (1.4) the sulphonation proceeds at about the same rate as that of "low sulphonated lignin", but that the fraction of lowest molecular weight contains more groups reactive towards sulphite than the average lignin. At higher pH-values (5.8) the rate of sulphonation is much higher in the case of the fraction of lowest molecular weight than of the remainder of the lignin.

The β-lignin sulphonic acids seem to contain about the same amount of phenolic hydroxyl groups as the remainder of the lignin.

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