Studies on the Sulphonation of Lignin. I *

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The fundamental reaction of the normal sulphite process is the sulphonation of lignin with formation of soluble lignin sulphonic acids. The pioneer work of Hägglund showed that a solid, insoluble lignin sulphonic acid is first formed [1]. Delignification takes place in later stages of the cook due to a hydrolytic process accompanied by further sulphonation. In this way, lignin sulphonic acids are obtained containing about one sulphonic acid group per two methoxyl groups.

So-called strong sulphite pulp still contains a considerable amount of solid, insoluble lignin sulphonic acids, generally in the form of calcium salts.

Kullgren found that the corresponding free acids, when heated with water or alcohols, are converted into water soluble acids [2]. This process is obviously due to a hydrolytic fission of linkages connecting neighbouring lignin molecules or lignin and carbohydrate molecules (in the strong pulp). The insolubility of the solid lignin sulphonic acid must be due to the presence of these large molecular complexes.

By sulphonating wood with strong solutions of sodium sulphites, possessing great buffer capacities and varying pH, Hägglund and Johnson were able to obtain low sulphonated wood containing far more solid, insoluble lignin sulphonic acids than strong pulp [3]. When subjected to the Kullgren process, they furnished large amounts of soluble low sulphonated lignin sulphonic acids. By variation of the pH of the sulphonation liquor, and stepwise performance of the Kullgren process, it is possible to obtain low sulphonated lignin sulphonic acids possessing varying contents of sulphonic acid groups. An additional advantage of this method is that the sulphonic acids are obtained in a state of high "purity". The largest portion of these acids can be preci-

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* Part 46 on the Chemistry of the Sulphite Process by E. Hägglund and co-workers.

pitated with 4,4'-bis-dimethylamino-diphenylmethane. "Low sulphonated lignin sulphonic acids" obtained in this way have been employed in this investigation and in various other recent studies in these laboratories [4].

When heated with ordinary sulphite cooking acid, the low sulphonated lignin sulphonic acids are rapidly converted into more highly sulphonated products. Ultimately, acids containing more sulphonic acid groups are formed than those generally obtained from ordinary technical waste liquors. This is apparently due to the mild conditions under which the acids have been prepared. It is possible to carry out the sulphonation stepwise. The ultraviolet absorption spectra of low, medium, and high sulphonated materials, with relation to the methoxyl content, have been found to be almost identical [4]. This shows that no double bonds which are conjugated with aromatic nuclei are formed or disappear during the sulphonation. No fundamental changes in the lignin structure appear to take place during this sulphonation, and it may be concluded that the low sulphonated lignin sulphonic acids contain non-sulphonated lignin elements of probably the same general structure as the original lignin in the wood. Hence, in these low sulphonated lignin sulphonic acids we apparently possess almost ideal materials for the investigation of the later stages of the sulphonation of lignin.

The nature of the groups responsible for the sulphonation reaction has been the subject of much speculation. Omitting the less probable suggestions, it is sufficient to mention only two.

Based on extensive analytical material, Holmberg concluded that the sulphonation essentially involves a substitution of sulphonic acid groups for hydroxyl groups of outstanding reactivity [5]. In α-phenethyl alcohol he found a suitable model substance [6]: C_6H_5—$CH(OH)$—$CH_3 \xrightarrow{H_2SO_3} C_6H_5CH(SO_3H)CH_3$. The yield and rate of reaction were, however, not very satisfactory. This may explain, at least partly, why Holmberg's idea has not been very generally accepted. In a recent review, v. Wacek, for instance, states that substitution of benzyl alcoholic hydroxyl groups can only account for a fraction of the total sulphonation of lignin [7].

Recently one of the present authors showed that more lignin-like analogues of Holmberg's α-phenethyl alcohol, e. g. vanillyl alcohol or veratryl alcohol or their homologues, undergo very facile conversions into the corresponding sulphonic acids [8], and the investigations were extended to complex ethers of the same type [9]. Hence the above mentioned objections to Holmberg's view are no longer valid. If this theory were correct, the sulphonation of lignin would be accompanied by a loss of hydroxyl groups.

Based on various considerations and model experiments, Freudenberg has

suggested a different mechanism. He assumes that the sulphonation of lignin is due to the fission of a heterocyclic ring followed by sulphonation [10]:

$$>C-O-C< \xrightarrow{\text{H}_2\text{SO}_3} >C-O-H \ (SO_3H)-C<$$
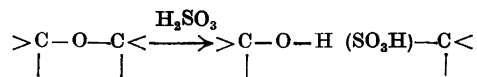
As a matter of fact, Freudenberg's view is related to that of Holmberg, since he assumes that the ring is of a benzyl ether type. Holmberg has shown that such ethers are cleaved by thioglycolic acid in a similar way [11].

If Freudenberg's theory were correct, the sulphonation of lignin should be accompanied by the liberation of one hydroxyl group for every sulphonic acid group introduced.

In several papers and reviews, Freudenberg points out that both types of reactions may occur simultaneously. However, he obviously considers the ring opening reaction to predominate, and in calculating the lignin composition from, for example, lignin sulphonic acids, he "prefers to subtract H_2SO_3" while Holmberg subtracts SO_2 [12].

It was originally supposed that a phenolic hydroxyl group is formed when the ring is opened. Later Freudenberg, Lautsch, and Piazolo obtained results which were difficult to reconcile with this assumption [13]. Instead they suggested that a tetrahydrofurane ring, of the type occurring in pinoresinol, is cleaved. However, pinoresinol and its alkyl ethers have not been found to react with the formation of sulphonic acids under the conditions of the normal sulphite cook [14].

The authors have attempted to settle the question of the appearance or disappearance of hydroxyl groups when sulphonic acid groups are introduced into the lignin molecules, by following analytically the changes in hydroxyl content when low sulphonated lignin sulphonic acids are progressively sulphonated. It is clear that from such studies nothing can be said about the mechanism of the introduction of the sulphonic acid groups already present in the low sulphonated lignin sulphonic acids employed. The experimental results described below cover about fifty per cent of the reactive groups in lignin, and this may perhaps indicate that the conclusions may be extended to include, at least, most of the active groups in the lignin molecules.

MATERIAL

The low sulphonated lignin sulphonic acids were prepared according to a method previously described [4]. They represent about twenty five per cent of the total lignin of the wood. Their sulphur content was approximately one sulphur atom per three C_{10}-elements (= three methoxyl groups), and they could be sulphonated to about one sulphur

atom per 1.4 C_{10}-elements. Part of the sulphur in these high sulphonated preparations is "loosely bound" — the amount of "alkali stable" sulphur being approximately one sulphur atom per 1.5 lignin elements. The recovery of lignin after resulphonations, based on methoxyl estimations, was about 60—75 per cent (compare Table 4).

HYDROXYL ESTIMATIONS

The acetylation method was selected for the estimations of the hydroxyl content of the various sulphonic acids.

The first problem was to find derivatives of lignin sulphonic acid suitable for acetylation. Sodium or barium lignin sulphonates could not be properly acetylated, mainly due to their insolubility in the acetylation mixture. The free lignin sulphonic acids are very unstable in the dry state. It was therefore considered advisable to avoid the use of desiccated acids.

Finally, it was found that the pyridine salts of the lignin sulphonic acids were fairly well suited for the purpose. Even in this case, however, it was difficult to obtain homogeneous reaction mixtures, and it was found necessary to repeat the acetylations three times in order to secure a constant acetoxyl content. Later investigations showed that this difficulty could be overcome by vigorous mechanical stirring of the reaction mixture. In this way some preparations were obtained containing slightly more acetoxyl groups than the corresponding ones obtained by repeated acetylations, but the difference is unsignificant (compare Tables 1 a and b).

First the well known acetylation method of Verley-Bölsing was tried. Due to various reasons, e. g. the difficulty to obtain perfectly dry starting material, the retention of acetic acid within the gelatinous acetylation product, and, especially in the case of high sulphonated lignins, the loss of some sulphur during the acetylation, this method had to be abandoned. It was also attempted to measure the increase in equivalent weight, caused by the acetylation, by means of potentiometric titrations, but this method also failed for similar reasons.

Finally, it was found that the isolated acetylated pyridinium salts could be analysed according to Clark [15] with reproducible results. The preparations were deacetylated with alkali and the acetic acid recovered by steam distillation of the acidified solution. Some sulphur dioxide was simultaneously formed and had to be taken into consideration.

RESULTS AND DISCUSSION

Table 1 gives the composition of the barium salts of four different lignin sulphonic acids (A, B, C, and D). The last three were obtained by successive sulphonation of acid A.

A Ac, B Ac, C Ac, and D Ac are the corresponding acetylated pyridinium salts.

Table 1. Analyses of barium salts of the lignin sulphonic acids A, B, C, and D, and of the pyridinium salts of the corresponding acetylated lignin sulphonic acids (A Ac, B Ac, C Ac, and D Ac).

Ba-salt of	A		B		C		D	
Pyridinium salt		A Ac		B Ac		C Ac		D Ac
%								
CH_3O	13.06	10.96 $(10.5)^{[1]}$	12.73	10.25 $(10.9)^{[1]}$	11.58	10.18 $(9.7)^{[1]}$	9.75	9.34 $(8.4)^{[1]}$
S	4.19	3.07	5.73	3.54	5.74	4.18	8.24	6.12
Ba	9.2	—	10.9	—	13.1	—	19.8	—
N	—	1.22	—	1.47	—	1.94	—	2.50
C	53.3	57.9	51.2	58.6	47.6	57.7	40.2	52.6
H	4.79	5.32	4.54	5.27	4.28	5.15	3.62	4.84
CH_3COO	—	26.6	—	23.9	—	21.0	—	15.4
S (loosely bound)	0.1	—	—	—	0.18	—	0.68	—
$\dfrac{S}{OCH_3}$	$\frac{1}{3.3}=0.30^{[2]}$	$\frac{1}{3.7}=0.27$	$\frac{1}{2.3}=0.44$	$\frac{1}{3.0}=0.33$	$\frac{1}{2.2}=0.46^{[2]}$	$\frac{1}{2.5}=0.40$	$\frac{1}{1.3}=0.75^{[2]}$	$\frac{1}{1.6}=0.63$
$\dfrac{Ba}{2S}$	$\frac{1}{0.98}=1.02$		$\frac{1}{1.13}=0.89$		$\frac{1}{0.94}=1.07$		$\frac{1}{0.89}=1.12$	
$\dfrac{N}{S}$		$\frac{1}{1.10}=0.91$		$\frac{1}{1.05}=0.95$		$\frac{1}{0.94}=1.06$		$\frac{1}{1.07}=0.93$
$\dfrac{CH_3COO}{OCH_3}$		1.28		1.23		1.08		0.87
$\dfrac{S+CH_3COO}{OCH_3}$		1.55		1.56		1.48		1.50

[1] Calculated value based on the methoxyl and barium content of the original salt and the acetoxyl content of the acetylated pyridinium salt. The formation of a small amount of sulphur dioxide during the acetylation was ignored.

[2] "Loosely bound" sulphur is subtracted.

Table 1 a. Control acetylations of the pyridinium salt of preparation A with strong mechanical stirring. Analyses of pyridinium salts.

Time of acety- lation. Hours	3	6	9	3	6	9	3	6	9	3	6	9
Per cent acetic anhydride in the acetylation mixture	10			50			10			50		
Temperature	100°			100°			50°			50°		
OCH_3 per cent	10.35	10.33	10.30	10.43	10.30	10.17	10.41	10.37	10.42	10.57	10.51	10.41
CH_3COO per cent	25.0	26.2	26.1	24.9	25.5	25.8	16.2	20.6	20.7	15.1	16.9	20.9
$\dfrac{CH_3COO}{OCH_3}$	1.27	1.33	1.33	1.25	1.30	1.33	0.82	1.04	1.04	0.75	0.85	1.06

Table 1 b. Control acetylations of the pyridinium salt of preparation D with strong mechanical stirring. Analyses of pyridinium salts.

Time of acetylation Hours	6	9	6
Per cent acetic anhydride in the acetylation mixture	10	10	50
Temperature	100°	100°	100°
OCH_3 per cent	9.01	9.02	8.99
CH_3COO per cent	16.0	17.0	16.6
$\dfrac{CH_3COO}{OCH_3}$	0.93	0.99	0.97

From Table 1 (last line) it can be seen that the number of sulphonic acid groups plus hydroxyl groups per methoxyl group is practically constant (1.48—1.55) in the various sulphonic acids. Under the assumption that no obscuring rearrangements occur during the sulphonation process (this assumption appears to be probable in view of the constancy of the ultraviolet absorption) this result shows that the sulphonation is mainly due to a substitution of a hydroxyl group by a sulphonic acid group.

The average, 1.52, of the quotients of the last line in Table 1 also represents the number of hydroxyl groups per methoxyl in the "original lignin" (S = nil), if it is assumed that no extrusion of water took place when the low sulphonated acid A was formed.

When comparing the quotients sulphur : methoxyl in Table 1, it is seen that the acetylation of each preparation is accompanied by the expulsion of a certain amount of sulphur. The amount is not particularly great, but large enough to exceed the amount of "loosely bound sulphur" present in the preparations. About 0.1 sulphur atom is expelled per methoxyl group in all cases except for the preparation with the lowest degree of sulphonation, from which only very little sulphur is split off.

In Table 2, the atomic composition of the lignin sulphonic acids is given on the customary C_9-basis. The values are calculated from the analyses given in Table 1. (OH calculated from the acetylated pyridinium salts, assuming that no methoxyl groups disappear on acetylation; other calculations based on the corresponding barium salts.) In Table 2 (a) it has been assumed that the sulphonic acid groups expelled during the acetylation have been exchanged for acetoxyl groups, and in (b) that no other groups were introduced when the sulphonic acid groups were extruded.

Table 2. Atomic composition of lignin sulphonic acids.

Sulphonic acid	C	H		OCH$_3$	$-O-$		OH		SO$_3$H
		a	b		a	b	a	b	
A	9	6.6	6.6	0.94	1.0	1.0	1.17	1.20	0.28
B	9	6.6	6.5	0.96	0.7	0.6	1.06	1.17	0.41
C	9	6.9	6.8	0.94	1.4	1.3	0.94	1.01	0.44
D	9	7.2	7.1	0.93	1.3	1.2	0.71	0.81	0.77

By substituting OH for SO$_3$H and calculating the average atomic composition of the "lignin" corresponding to the acids A—D in Table 2 (a), the following is obtained:
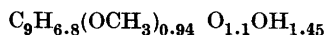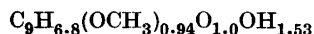
$$C_9H_{6.8}(OCH_3)_{0.94} \; O_{1.1}OH_{1.45}$$

Table 2 (b) gives in the same way:

$$C_9H_{6.8}(OCH_3)_{0.94}O_{1.0}OH_{1.53}$$

In an interesting study of the stepwise delignification of spruce wood with sulphite cooking acid at 70°, which has been briefly referred to above, Freudenberg, Lautsch, and Piazolo obtained a series of lignin sulphonic acids of increasing sulphur content. The corresponding free acids were desiccated at 55° and the hydroxyl contents estimated according to the method of Verley-Bölsing. From the analytical results recorded, the following average composition of these acids (OH instead of SO$_3$H) has been calculated:

$$C_9H_{7.0}(OCH_3)_{0.91}O_{0.76}(OH)_{1.58}$$
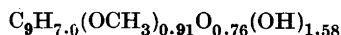
This formula agrees tolerably well with those of our preparations from low sulphonated lignin sulphonic acids.

It is of interest to compare these figures for the "lignin" from lignin sulphonic acids, with those for "lignin" obtained from various thiol acid lignins obtained by Holmberg in 1942 [5]. (Holmberg gives no figures for hydroxyl.) He finds the following average composition:

$$C_9H_{8.91}(OCH_3)_{0.92}O_{2.85}$$

The corresponding figures calculated from Table 2 (a or b) are:

$$C_9H_{8.2}(OCH_3)_{0.94}O_{2.5}$$

This composition agrees fairly well with that of Holmberg's preparations, if it is assumed that the "lignin" from the lignin sulphonic acids contains approximately 0.3 H_2O per C_9-unit less than that from Holmberg's thiol acid lignins.

Peniston and McCarthy dialyzed technical waste sulphite liquor and obtained preparations of the following compositions [16]:

$$C_9H_{7.2}(OCH_3)_{0.94}O_{2.75}$$

$$C_9H_{7.0}(OCH_3)_{0.95}O_{2.84}$$
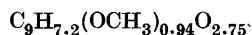
The composition of these lignins differs considerably from those reported above — the hydrogen figures being remarkably low in spite of the high oxygen content.

We have also calculated the quotients sulphur : methoxyl and hydroxyl : methoxyl as well as (sulphur + hydroxyl) : methoxyl in the various sulphonic acids of Freudenberg and his collaborators and the result is shown in Table 3.

Table 3. Relations of sulphur, hydroxyl, and sum of sulphur and hydroxyl to methoxyl in a series of lignin sulphonic acids of increasing sulphur content prepared by Freudenberg, Lautsch, and Piazolo.

Sulphonic acid preparations	1	2	3	4	5	6	7	8
S/OCH_3	0.51	0.47	0.48	0.56	0.70	0.84	0.96	1.50
OH/OCH_3	1.25	1.30	1.18	1.11	1.09	0.99	0.88	0.95
$(S + OH)/OCH_3$	1.76	1.77	1.66	1.67	1.79	1.83	1.84	2.45

The sum of sulphonic acid and hydroxyl groups is constant also in this series of sulphonic acids. Only the last preparation (8) is distinctly different. This material, however, was obtained in a minute yield and represents only about one per cent of the total lignin of the wood. The results of Freudenberg, Lautsch, and Piazolo are in accordance with the view that lignin is sulphonated essentially by substitution of hydroxyl groups by sulphonic acid groups.

EXPERIMENTAL

Resulphonation of low sulphonated lignin sulphonic acids

A sample of the barium salt of A, (Table 1) corresponding to 4.4 g dry barium salt, was dissolved in water and the solution passed through a cation exchanger ("Wofatit K") saturated with hydrogen ions. Calcium carbonate (1.5 g) was added to the filtrate, and

the volume made up to 100 ml. Sulphur dioxide was passed through the solution until the total amount of sulphur dioxide was about 5 per cent. The solution was heated in a sealed tube at 135° for various lengths of time. The sulphonic acid preparations B, C, and D (Table 1) were obtained in this way from A by heating 1 ¼ hours (B), 2 hours (C), and 10 hours (D).

The tubes were opened, nitrogen passed through the solutions until almost all free sulphur dioxide had been driven off, the calcium ions exchanged for hydrogen ions by means of passage through Wofatit K, nitrogen again passed through the solution to remove sulphur dioxide, and finally barium carbonate added to neutralize the solution. This was filtered, concentrated in a vacuum to about 50 ml, refiltered or centrifuged from a small amount of barium sulphite, and the clear solution poured into five volumes of alcohol. The precipitated barium lignin sulphonates were collected by centrifuging, washed several times with alcohol, and finally with ether. For analysis the samples were dried at 80° in a vacuum over P_2O_5 until constant weight was reached (about seven days). The recovery of lignin based on methoxyl estimations was somewhat varying — generally about 70 per cent. (For examples compare Table 4.)

Table 4. Yield of high sulphonated lignin sulphonic acids on sulphonation of low sulphonated lignin sulphonic acids.

Low sulphonated lignin sulphonic acid. Ba-salt		Cooking acid		Time of heating at 135°, hours	High sulphonated lignin sulphonic acid. Ba-salt		
g	S/OCH$_3$	ml	% SO$_2$		Yield g	S/OCH$_3$	% yield based on OCH$_3$
4.4	0.37	100	5.2	1.5	2.8	0.46	63
4.4	0.37	100	6.8	3.0	3.8	0.64	76
4.4	0.37	100	7.0	6.0	3.3	0.62	66
4.1	0.31	100	7.6	0.75	3.6	0.37	75
4.2	0.31	100	8.0	10.0	3.5	0.82	66

Preparation of pyridinium salts of acetylated lignin sulphonic acids

By repeated acetylation (Table 1): Water solutions of the barium salts of the acids A—D were passed through hydrogen ion saturated Wofatit K and the filtrates neutralized with pyridine. The solutions were evaporated over sulphuric acid in vacuum desiccators. The dry material was powdered, and ten times its weight of acetylation mixture (10 per cent solution of acetic anhydride in pyridine) was added. After 24 hours at room temperature (for swelling), the mixture was heated for three hours in boiling water in a flask fitted with a calcium chloride tube. Ether was then added and the precipitated, acetylated pyridinium salt was powdered under ether, carefully washed with ether, collected, and dried to constant weight in a vacuum desiccator over sulphuric acid. The drying required a long time (about three weeks). In order to obtain completely acetylated products th⌐ acetylation procedure was repeated 3—4 times.

By acetylation with stirring (Tables 1 a and 1 b.): 0.5 g of the pyridinium salts of the lignin sulphonic acids A and D were added to acetylation mixtures (10 ml) containing pyridine and acetic anhydride in the proportions 1 : 1, resp. 9 : 1. The mixtures were heated at 50 or 100° for varying times with efficient mechanical stirring. The low sulphonated material (A) dissolved completely in the acetylation mixture. The highest sulphonated preparation (D) failed to yield a perfectly clear solution. The acetylated products were isolated by precipitation with ether.

Estimations of acetoxyl groups

The method of Clark was employed [15]. The saponification, however, was carried out with 1 N aqueous, instead of alcoholic, potassium hydroxide, because the preparations were more soluble in water than in alcohol. Some sulphur dioxide passed over together with the acetic acid. The distillate was therefore titrated with 0.03 N barium hydroxide to get the sum of acetic and sulphurous acid. Some hydrogen peroxide was then added and the water evaporated. The barium sulphate formed was collected by filtration and weighed.

The correction for sulphur dioxide was equal to about 1—2 % acetoxyl groups.

SUMMARY

Low sulphonated lignin sulphonic acids have been subjected to stepwise sulphonation with ordinary sulphite cooking acid. By acetylation of the pyridinium salts of the various lignin sulphonic acids obtained and complete analysis of the preparations, it has been found that for each sulphonic acid group introduced into the low sulphonated lignin sulphonic acid about one hydroxyl group disappears.

It is concluded that, at least in the later stages of the sulphonation of lignin, the sulphonation involves the substitution of hydroxyl groups of outstanding reactivity. The experiments cover approximately fifty per cent of the groups which become sulphonated.

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