Studies on the Cooking Mechanism of Wood. XII[1]*. On the Nature of the weakly Acidic Group of Lignosulphonic Acid*

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It is a well known fact that the sulphite spent liquor shows considerable buffering action for neutralization. This phenomenon is clearly shown by the conductometric titration of the waste liquor. Among others, investigations of Hachihama[2], Samuelson[3], and Adler[4] made clear that this buffering action is due to the presence of sulphurous acid, organic acids, i.e. formic, acetic etc., so called loosely combined sulphurous acid, and some weakly acidic group of lignosulphonic acid itself. As the elucidation of the nature of the weakly acidic group of lignosulphonic acid is very interesting not only from the scientific, but also from the technical point of view, we will deal with this problem in the present communication.

It has been open to question, whether this group, which amounts to approximately one equivalent per 4–5 methoxyl groups, is carboxylic or phenolic in nature. Hachihama et al. assumed this to be phenolic, and Samuelson supposes that this may be carboxylic. As both carboxyl and phenolic hydroxyl groups are usually methylated by diazomethane to ester and phenol-ether groups respectively (some exceptions exist however : for example phenolic hydroxyl groups of conidendrin[5], and 3,3'-

1) Part XI, Preceeding Paper, p. 649.

2) Y. Hachihama, H. Shinra and Y. Kyogoku, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **47**, 209, 212 (1944).

3) S. Regestad and O. Samuelson, *Svensk Kem. Tid.*, **61**, 9 (1949).

4) E. Adler, *Svensk Papperstidn.*, **50**, 261, No. 11B 9 (1947).

5) F. Brauns, *J. Org. Chem.*, **10**, 216 (1945).

dimethoxy-4.4'-dihydroxy diphenylmethane[6]) were not methylated by diazomethane), it is expected that such a weakly acidic group must disappear after the methylation, and must reappear by alkaline hydrolysis, if the methylated group were carboxyl. Hachihama and Kyogoku observed recently that the weakly acidic group of lignosulphonic acid disappeared by methylation with dimethyl sulphate[7]).

α-Lignosulphonic acid of spruce origin (lignosulphonic acid A, $S/CH_3O=0.44$) has a considerably large weakly acidic group (one equivalent per 4.7 CH_3O), as is evident from curve I Fig. 1, but this group disappears

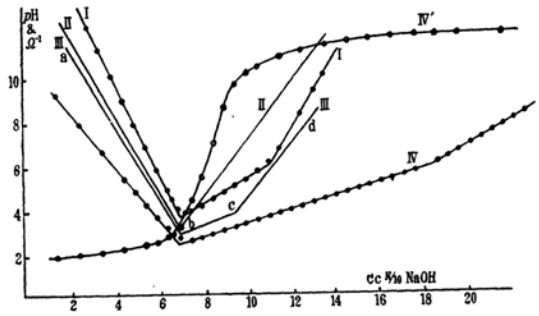

Fig. 1. Conductometric titration of lignosulphonic acid A (I), diazomethylated lignosulphonic acid A (II), diazomethane methylated lignosulphonic acid A after hydrolysis in nitrogen atmosphere at 30° for 72 hr. in 1 N NaOH (III) (Absorption spectra taken at a, b, c and d are shown in Fig. 2.) and the cond. and potent. titrations of lignosulphonic acid A after being kept in 1 N NaOH for 48 hr. at 30° in a closed vessel with air (IV, IV').

after methylation with diazomethane (curve II). This weakly acidic group which once disappeared was regenerated more than 50% after mild alkaline hydrolysis in nitrogen atmosphere, the hydrolysis condition being selected so as to be sufficient to hydrolyze ferulic acid methyl ester completely, i.e. 1 N NaOH, 30°C, 72 hr., for the reasons to be mentioned later (curve III). This result will most easily be explained by assuming that more than 50% of the weakly acidic group consists of carboxylic acid group. The diazomethylated lignosulphonic acid A shows completely the same UV-absorption in neutral and alkaline media (I, Fig. 2), which fact indicates that all phenolic hydroxyl groups are completely methylated. The UV-absorption curves were taken at point a,b,c and d of the conductometric titration curve of

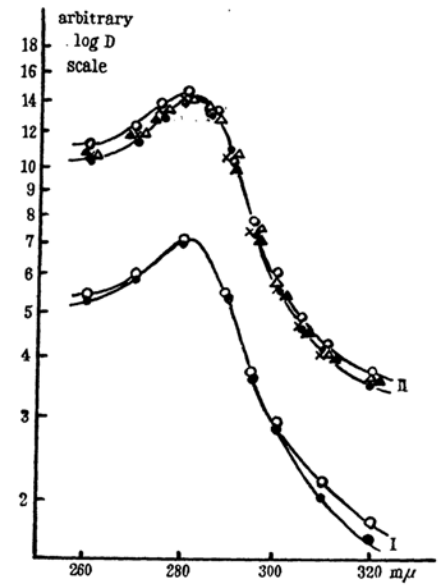

Fig. 2. Absorption spectra of diazomethylated lignosulphonic acid A (I) (● neutral, ○ 1 N NaOH) and of the diazomethylated lignosulphonic acid A after hydrolysis measured at points a, b, c and d of the conductometric titration (curve III, Fig. 1) (II) (● a, × b, ▲ c, △ d, ○ 1 N NaOH).

hydrolyzed diazomethylated lignosulphonic acid A (III, Fig. 1), without any dilution using a very thin cell. All curves superpose each other (II, Fig. 2), indicating that the phenolic hydroxyl group does not exist even after the hydrolysis. The weakly acidic group of this acid must, therefore, be carboxyl in nature. Even a slight increase in the number of weakly acidic group was not observed after keeping lignosulphonic acid A in 1 N sodium hydroxide for two days, and four days, at 30°C in nitrogen atmosphere. The carboxylic acid group observed after the hydrolysis of the methylated lignosulphonic acid must, therefore, be formed from the methylated carboxyl group by hydrolysis, and can not be a carboxylic acid group newly formed by oxidation during the hydrolysis.

Diazomethylation is able to be substituted by the methylation with dimethyl sulphate, as is shown in Fig. 3. Here, the conductometric and potentiometric titrations of another sample of α-lignosulphonic acid (lignosulphonic acid B, $S/CH_3O=0.49$) (curves I and I', Fig. 3), conductometric tritration of this acid after methylation with dimethylsulphate (II, Fig. 3), and the conductometric, and potentiometric titrations of this methylated lignosulphonic acid, after hydrolysis for two-

6) I. Pearl, *J. Am. Chem. Soc.*, 68, 429 (1946).
7) Y. Hachihama and Y. Kyogoku, *Technology Reports of the Osaka Univ.*, 3, 375 (1953).

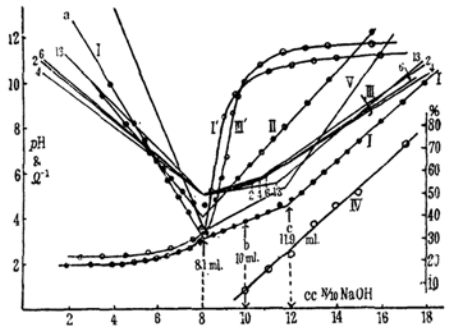

Fig. 3. *Conductometric and potentiometric* titration of lignosulphonic acid B (I, I') (Absorption spectra are shown in Fig. 4.), cond. titr. after methylation with dimethyl sulphate (II), cond. titr. of methylated acid after hydrolysis for 2–13 days at 30° in 1 N NaOH (III) and the potent. titr. after hydrolysis for 6 days (III'), percentage of the phenolic hydroxyl group ionized during the cond. titr. of lignosulphonic acid B along the curve I (IV) and the cond. titr. of sodium borohydride reduced lignosulphonic acid B (V).

thirteen days are shown (curves III and III', Fig. 3). The results are completely the same as in the case of diazomethylation mentioned above. This is quite understandable, as many examples are reported telling that the carboxyl group is esterified with dimethyl sulphate and alkali, for example, methylester from stearic acid[8], campholic acid[9], gallic acid[10] etc. More than 50% of the weakly acidic group seems again to be carboxyl in nature.

During the conductometric titration of the lignosulphonic acid B (Fig. 3, I), one drop of the solution was taken out at various points, and the UV-absorption of these solutions was measured without any dilution, using a very thin cell in order not to shift the condition of ionization of the lignosulphonic acid at these points. The UV-absorption curves thus obtained must therefore represent the condition of the lignosulphonic acid molecule at every stage of the titration. No change of the adsorption was observed from point "a" (free lignosulphonic acid) to "b" (half way of the weakly acidic part, titrant added, 10 ml.), corresponding to the neutralization of sulphonic acid group and the ionization of carboxyl group, which may not affect the absorption appreciably. After this point, the absorbancy at about 300 mμ rises slowly, and this rise is shown clearly by $\Delta\varepsilon$ curves of Fig.

8) A. Werner and W. Seybold, *Ber.*, 37, 3559 (1904).
9) J. Riedel, D.R.P. 187840, 196152.
10) P. Graebe and H. Martz, *Ann. d. Chem.*, 340, 219 (1905).

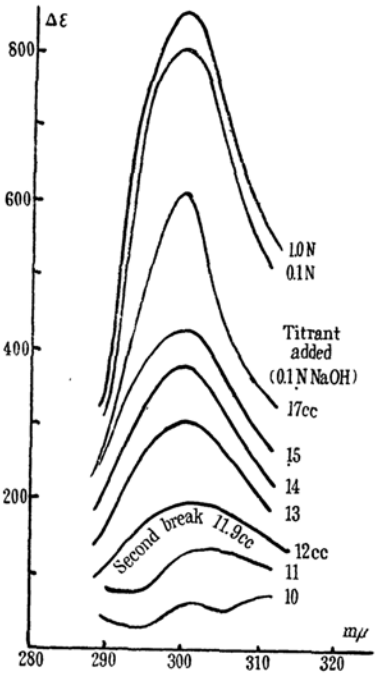

Fig. 4. Difference of the free acid spectrum and the spectra taken at various points of the conductometric titration of lignosulphonic acid B (cf. Fig. 3, Curve I).

4. $\Delta\varepsilon$ values were obtained by subtracting the absorption curve for point "a" from those for other points. Here in this figure, only the values obtained between 290 mμ to 310 mμ are shown. According to Aulin-Erdtman[11], the increase of the absorption at about 300 mμ is attributable to the ionization of the phenolic hydroxyl groups, and the total amount of the phenolic hydroxyl group is proportional to the difference of ε values, taken at 300 mμ in acidic or neutral and strong alkaline (1 N) media. $\Delta\varepsilon$ values obtained in 0.1 N and 1 N sodium hydroxide is also shown in Fig. 4. The increase of $\Delta\varepsilon$ value from the half way of the weakly acidic part of the conductometric titration, i.e. point "b" to the second "break" (point "c", titrant added, 11.9 ml.), is only about 24% of the $\Delta\varepsilon$ value which corresponds to the total amount of the phenolic hydroxyl groups ionizable in 1 N alkalinity. The percentage of the ionized phenolic hydroxyl groups during the titration thus obtained, is shown by curve IV of Fig. 3. Thus, one may be able to deduce also from such spectroscopic considerations, that about 50–75% of the weakly acidic group may be carboxyl, and the remaining 50–25% rather strong phenolic hydroxyl group.

11) G. Aulin-Erdtman, *Svensk Papperstidn.*, 55, 745 (1952); 56, 91, 287 (1953).

Aqueous solution of vanillyl sulphonic acid was titrated conductometrically, and at the same time UV-absorption spectra were measured in the same manner as in the case of lignosulphonic acid. As seen from Fig. 5, the ionization of its phenolic hydroxyl group

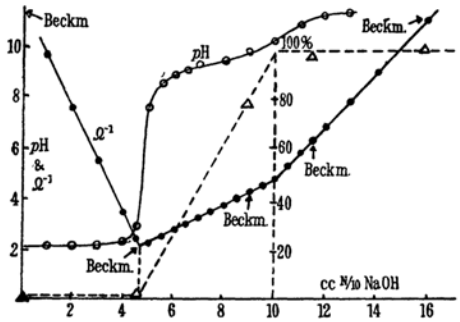

Fig. 5. Conductometric and potentiometric titrations of vanillyl sulphonic acid and the spectroscopically estimated percentage of the ionized phenolic hydroxyl group. Beckm. means the measurement of absorption by Beckmanspectrophotometer at the indicated points.

was complete already at the second "break". From this fact it may be certain that the phenolic hydroxyl group of the lignosulphonic acid, titrated before the second "break", must have been ionized before the "break", and the remaining part, which did not ionize before the second "break", did not contribute to the weakly acidic part of the conductometric titration.

As mentioned earlier, even up to 80–90% of the weakly acidic group was regenerated after prolonged hydrolysis. Judging from the amount of the spectroscopically estimated phenolic hydroxyl group, which contributed to the weakly acidic group of the lignosulphonic acid, however, it seemed improbable that so much carboxyl group existed in lignosulphonic acid. Lignosulphonic acid is very susceptible to oxidation in alkaline medium, which is clearly shown by curve IV of Fig. 1. Here, it is shown that the amount of the weakly acidic group of lignosulphonic acid A increases very much, after being kept in 1 N sodium hydroxide for forty eight hours at 30°C in a closed vessel with air. As lignosulphonic acid is so susceptible to oxidation, it may not be impossible that a slight increase of carboxylic acid group occurs, even in the case of the hydrolysis in nitrogen atmosphere.

The phenolic hydroxyl group, titrated before the second "break", must be stronger than the remaining phenolic hydroxyl groups. As the phenols with carbonyl group, conjugated with a benzene ring, in its para position are generally very strong, the lignosulphonic acid B was titrated conductometrically after the reduction with sodium borohydride. The amount of the weakly acidic group did not decrease appreciably by the reduction. The titration curve and the UV-absorption are shown by curve V of Fig. 3 and by Fig. 6 respectively.

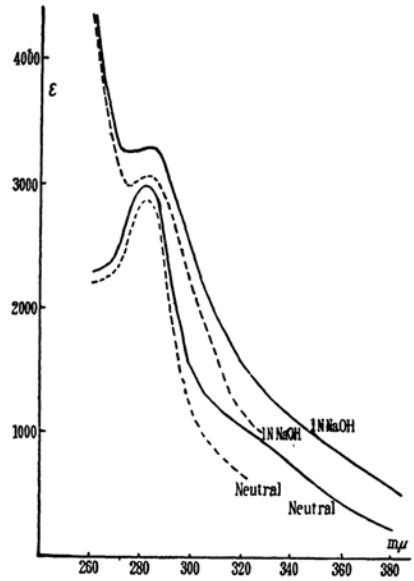

Fig. 6. UV-absorption spectra of lignosulphonic acid B (——) and sodium borohydride reduced lignosulphonic acid B (----).

Only lignosulphonic acids prepared from spruce were investigated so far, but the acids prepared from birch and beech have also considerable amount of weakly acidic group, the conductometric and potentiometric titration curves of these acids being essentially the same with the acids of gymnosperm origin. Since the lignosulphonic acid is very easily oxidized by air in alkaline solution as mentioned above, it will naturally be suspected, if the weakly acidic group is formed by air oxidation, during the isolation and purification, when the acid is treated with alkali. In order to confirm this, the birch lignosulphonic acid was isolated and purified without using alkali. during the whole process; i.e. after dialysis and ion exchange of the waste liquor, the lignosulphonic acid was precipitated by 1-(N-piperidino- acetylamino)-naphthalene as usual, the precipitate was dissolved in aqueous acetone containing some amount of sulphuric acid, the solution passed through IR 120 in hydrogen form, and the eluate was neutralized by barium carbonate. The lignosulphonic acid thus prepared had,

however, a weakly acidic group as indicated in Fig. 7.

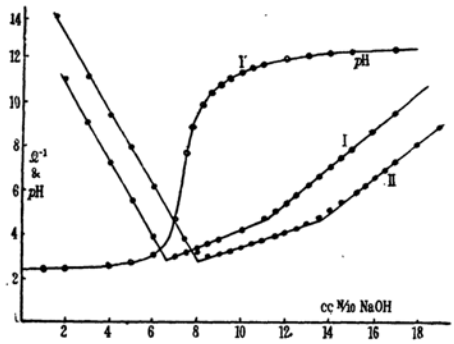

Fig. 7. Conductometric and potentiometric titration of birch lignosulphonic acid (I, I') and cond. titr. of beech lignosulphonic acid isolated and purified without being kept alkaline during the preparation (II).

Analytical data of the lignosulphonic acids used, are listed in Table I. Taking example acid A increased from 11.97% to 16.86% by methylation with diazomethane. The difference, 4.89%, must correspond to the methoxyl group mainly introduced to the phenolic hydroxyl group and the carboxyl group. If one neglects a slight increase of weight by methylation, the value of $\Delta CH_3O/CH_3O$ is about $0.4/CH_3O$. As the amount of the phenolic hydroxyl group must be much less, one must assume the existence of carboxyl group from such a point of view too.

Discussion

The existence of a carboxyl group in lignin and lignosulphonic acid was advocated by some authors, but many others could not recognize it[12]. Friedrich and Diwald[13], and Moore, Wright and Hibbert[14] recognized a little amount of methyl ester group in alcohol lignin. Phillips[15] thought to have recognized carboxyl group in corncob lignin. On the basis of analytical composition of lignosulphonic acid salts, Hönig and Fuchs[16], and

TABLE I

ANALYSES OF LIGNOSULPHONIC ACIDS

lignosulphonic acid	Anal. S%	Cond. SO_3H S%	weakly acidic group equiv./C_9	CH_3O	SO_3H/C_9	spectroscopically measured OH*/C^9
A 1)	6.81	5.45	one/4.7	11.97	0.47	—
after CH_2N_2 methylation	5.63	5.10	zero	16.86	—	zero
B 2)	6.67	5.76	one/4.8	11.32	0.51	0.21–0.17
after methylation with $(CH_3)_2SO_4$	—	5.34	zero	16.70	—	zero
beech 3)	6.90	5.76	one/2.5	15.01	0.56	—
birch 4)	8.00	4.75	one/3.5	15.20	0.53	0.26–0.21

1) $C_9H_{10.4}O_{2.77}(CH_3O)_{1.06}(SO_3Ba/2)_{0.47}S^{neut.}_{0.12}Ba^{excess}_{0.04}$

2) $C_9H_{10.7}O_{3.2}(CH_3O)_{1.05}(SO_3Ba/2)_{0.51}S^{neut.}_{0.08}Ba^{excess}_{0.04}$

3) $C_9H_{9.82}O_{3.25}(CH_3O)_{1.53}(SO_3Ba/2)_{0.56}S^{neut.}_{0.11}Ba^{excess}_{0.05}$

4) $C_9H_{9.35}O_{2.87}(CH_3O)_{1.40}(SO_3Ba/2)_{0.53}S^{neut.}_{0.36}Ba^{excess}_{0.04}$

in the lignosulphonic acid B, this acid contains 0.04 mol. excess barium per C_9, which is not combined with the sulphonic acid group, and one equivalent weakly acidic group per 4.8 CH_3O, i.e. 0.22 equivalent per C_9 unit. Provided that the excess barium is combined with the carboxyl group, it is calculated from these data that the carboxyl group amounts to about 36% of the weakly acidic group. It will, however, be possible that only a part of the carboxyl group is neutralized with barium, as the neutralization was performed with barium carbonate, and the carboxyl group seems to be a very weak one.

As can be seen from Table I, the content of the methoxyl group of the lignosulphonic

Klason[17] thought to have recognized carboxyl group in some lignosulphonic acid preparations. Some barium salt had Ba/S values slightly higher than 0.5. Freudenberg et al.[18] reports that the lignosulphonic acid, prepared at relatively low temperature of 70°C, contained 1.8–2.8% of carboxyl groups.

12) Y. Hachihama and S. Jodai, "Chemistry of Lignin", Nihonhyoron Press., Tokyo (1946), p. 391.
13) A. Friedrich and J. Diwald, *Monatsh.*, **46**, 31 (1925).
14) R. Moore, G. Wright and H. Hibbert, *Can. J. Res.*, **15B**, 532 (1937).
15) M. Phillips, *J. Am. Chem. Soc.*, **53**, 768 (1931).
16) M. Hönig and W. Fuchs, *Monatsh.*, **41**, 215 (1920).
17) P. Klason, *Ber.*, **53**, 1864 (1920); **55**, 455 (1922); **56**, 300 (1923).
18) K. Freudenberg, W. Lautsch and G. Piazolo, *Cellulosechem.*, **22**, 97 (1944).

Kullgren[19] reports recently that the lignosulphonic acid in unbleached sulphite pulp seems to have carboxyl group. With many lignin preparations it is recognized, however, that Ba/S is practically 0.5, which fact was thought to suggest that the preparations did not contain carboxyl groups[20]. However, as Samuelson and Westlin[21] found that lignosulphonic acid contained a little amount of non-acidic sulphur, which he called "excess sulphur", one can not attribute the apparent equivalence of barium and sulphur in the lignosulphonic acid, directly to the non-existence of the carboxyl group.

As lignin contains cinnamic aldehyde side chain, $-CH=CH-CHO$, although in very limitted amount[22], it may not be improbable that a part of such a group is oxidized to cinnamic acid group, $-CH=CH-COOH$, just as the formation of aldonic acid from aldose, during the cooking reaction[23]. It may, however, be quite impossible, to ascribe so much carboxyl group as one per 8–9 methoxyl observed in α-lignosulphonic acid, to such origin, as reportedly, the amount of cinnamic aldehyde side chain is so little as one per about 50 methoxyl, and, moreover, this group survives at least partly even after the sulphonation reaction. The carboxyl group of cinnamic acid type was, however, assumed tentatively in the present communication, and ferulic acid methyl ester was used to determine the condition of the hydrolysis, as was described previously. It remains open to question whether the carboxyl group exists even in lignin in situ, or it is formed during sulphonation. This fact will be a problem to be investigated in future.

The amount of the conductometrically titrable phenolic hydroxyl group was found to be only about 1/3–1/4 of the total phenolic hydroxyl group. The titrable one must be stronger than the remaining one. It is reported that phenolic hydroxyl group with carbonyl group in its para position is very strong in comparison with ordinary phenols. Some examples are listed in the Table II. Some of them are so strong that they are

TABLE II

pK OF SOME PHENOLS[23]

phenols	pK
α-hydroxypropiovanillone	7.32
α-hydroxypropiosyringone	7.45
acetovanillone	7.50
guaiacol	9.55
phenols	9.60

comparable to nitrophenols. According to Goldschmid[24] and Aulin-Erdtman[25], phenolate ion with carbonyl group in its para position, shows intensive absorption at about 350 mμ, which is so strong that even so little amount as one such group per 50 methoxyl is spectroscopically still measurable. Although the absorption curves of our lignosulphonic acid do not show any clear maximum at this wave length in alkaline medium, as were shown in Fig. 6, considerable decrease of absorption was observed after reduction with sodium borohydride, which is sufficient to reduce such carbonyl group, if any[26]. The amount of the weakly acidic group of the lignosulphonic acid did not, however, decrease appreciably by the reduction. One can not, therefore, expect much contribution of such phenolic hydroxyl group with carbonyl group in its para position to the weakly acidic group.

As an example of the other type of strong phenolic hydroxyl group, one can cite the report of Sprengling[27]. According to him one of the phenolic hydroxyl groups of o,o'-dihyroxydiphenyl methane is very strong due to the hydrogen bonding of one of the two phenolic hydroxyl groups to the oxygen atom of the other resulting in an enhanced ionization of the hydrogen atom of the latter hydroxyl group. On the other hand Aulin-Erdtman recognizes that one of such phenolic hydroxyl groups is rather weak in comparison to the ordinary phenols[11,25]. Such diphenylmethane structure may not be so feasible to lignin structure.

According to her one of the phenolic hydroxyl groups, which belong to o,o'-diphenol, is very strong, and the remaining one is very weak. Such very strong phenolic hydroxyl group must have been titrated, if it existed in lignosulphonic acid, The existence of diphenyl structure in lignin is not, however, established as yet. The fact that

19) C. Kullgren, *Svensk Papperstidn.*, 55, 1 (1952).
20) H. Erdtman, *Svensk Papperstidn.*, 45, 315, 374, 392 (1942).
21) O. Samuelson and A. Westlin, *Svensk Papperstidn.*, 50, 141 (1947); 51, 179 (1948).
22) E. Adler, K. Björkqvist and S. Häggroth, *Acta Chem. Scand.*, 2, 93 (1948); E. Adler and L. Ellmer, ibid., 839; K. Kratzl, *Monatsh.*, 78, 173 (1948); T. Harada and J. Nikuni, *J. Agr. Chem. Soc. Japan*, 23, 415 (1950); J. Pew, *J. Am. Chem. Soc.*, 73, 1678 (1951); 74, 2850, 5784 (1952); T. Nakamura and S. Kitaura, *Bulletin of the Institute of Sci. and Ind. Research, Kyushu Univ.*, 8, 1 (1952).
23) E. Hägglund, *Ber.*, 62, 84 (1929); E. Hägglund and H. Urban, ibid., 2046; T. Marusawa, *Bulletin of the Ryojun Institute of Technology*, 1, 351 (1929).
24) O. Goldschmid, *J. Am. Chem. Soc.*, 75, 3780 (1953).
25) G. Aulin-Erdtman, *Svensk Papperstidn.*, 57, 745 (1954).
26) J. Gierer, *Acta Chem. Scand.*, 8, 1319 (1954); S. Chaikin and W. Brown, *J. Am. Chem. Soc.*, 71, 122 (1949).
27) G. Sprengling, *J. Am. Chem. Soc.*, 76, 1190 (1954).

dehydro-diveratric acid[28], dehydro-divanillic acid[29] and dehydro-divanillin[30] are obtained by permanganate oxidation, cupric oxide oxidation and oxidation with nitrobenzene respectively, can not prove definitely, the existence of such structure, as one may be able to ascribe the formation of such degradation products to the secondary formation during the oxidation. Its existence seems, however, to be quite probable. By nitrobenzene oxidation, Leopold obtained dehydro-divanillin from lignin, but not from model compounds with guaiacyl nucleus. Phenols without double bond conjugated with benzene nucleus in its para position dimerize easily resulting in the formation of o,o'-diphenol structure[31]. As Freudenberg's dimeric intermediates of the biosynthesis of lignin, i.e. d,l-pinoresinol[32], dehydro-diconiferyl alcohol[33], and β-coniferyl ether of guaiacylglycerol[34], have such guaiacyl groups, it seems to be quite probable that some of such guaiacyl groups condense by further dehydrogenation, at 5th position in the process of the formation of DHP.

Jodai titrated conductometrically isoeugenol and hydrolignin, which was prepared by mild hydrogenation of *picea jezoensis* with Raney nickel in alkaline medium[35]. By back titration, the phenolic hydroxyl group of isoeugenol was conductometrically titrated. The phenolic hydroxyl group of hydrolignin, which was confirmed to be almost only simple guaiacyl type was also titrable by back titration. As mentioned before, the phenolic hydroxyl group of vanillyl sulphonic acid was titrated quantitatively. It seems, therefore, to be certain that such simple phenolic hydroxyl group of guaiacole type, contained in lignosulphonic acid, contributes also to its weakly acidic group. Recently Gierer[25] proved definitely that Brauns' native lignin as well as lignin in situ, contain about one 3-methoxy-4-hydroxy-benzyl alcohol type unit per seven to nine methoxyl groups.

More than half of the total amount of the phenolic hydroxyl group of lignosulphonic acid remains untitrated by conductometric titration. This phenolic hydroxyl group must be the weaker one. Hence, it appears that a comparatively small part of the total phenolic hydroxyl group belongs to simple guaiacol type. Recently Aulin-Erdtman have reported that phenolic hydroxyl group of guaiacyl nucleus with balky substituent at 5th position is rather weak. Such phenols were not ionized completely even at pH 12. In connection with the nature of the different phenolic hydroxyl groups of lignosulphonic acid, the conductometric titrations of various model compounds will be reported later.

28) K. Freudenberg, K. Engler, E. Flickinger, A. Sobeck and F. Klink, *Chem. Ber.*, **71**, 1817 (1938).
29) I. Pearl, *J. Am. Chem. Soc.*, **72**, 2309 (1950).
30) B. Leopold, *Acta Chem. Scand.*, **6**, 38 (1952).
31) H. Erdtman, *Biochem. Z.*, **258**, 172 (1933).
32) K. Freudenberg and H. Dietrich, *Chem. Ber.*, **86**, 4 (1953).
33) K. Freudenberg and H. Hübner, *Chem. Ber.*, **85**, 1181 (1952).
34) K. Freudenberg and W. Fuchs, *Chem. Ber.*, **87**, 1824 (1954).
35) S. Jodai, *J. Soc. Chem. Ind. Japan*, **47**, 958 (1944).
36) J. Fisher, W. Hawkins and H. Hibbert, *J. Am. Chem. Soc.*, **63**, 3031 (1941).

Experimental

Preparation of Ba-lignosulphonate, methylation with diazomethane or with dimethyl sulphate, and reduction with sodium borohydride.—Barium lignosulphonate was prepared from the waste liquor of experimental cooking of spruce and birch, just in the same manner as was used in the previous communication[1].

In the case of birch lignosulphonic acid, the precipitate obtained by 1-(N-piperidinoacetylamino)-naphthalene was dissolved in 70% aceton, 2 N sulphuric acid added, untill a clear solution was obtained, and the solution was passed through IR 120 in hydrogen form. Acetone was distilled off in vacuo, and the solution was neutralized with barium carbonate and treated further as usual.

Barium lignosulphonate was kept in an etherial solution of diazomethane with occasional shaking, and changing the solution four times during thirty days, until constant methoxyl content was reached.

Barium lignosulphonate was methylated with dimethyl sulphate and alkali as usual, and separated by 1-(N-piperidinoacetylamino)-naphthalene sulphate.

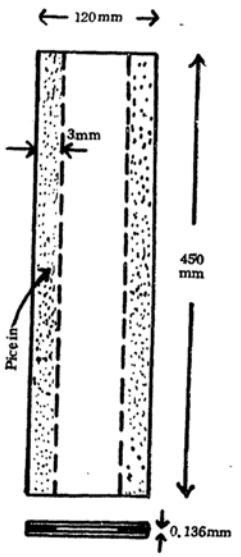

Fig. 8. Thin cell for UV-absorption mesurement.

Borohydride reduction of barium lignosulphonate was performed by dissolving the barium salt (15 g.) in water (200 ml.), adding sodium borohydride (2 g.), and keeping the solution at room temperature for four hours. The reduced barium lignosulphonate was precipitated by alcohol.

Hydrolysis.—Barium lignosulphonate (500 mg.) was dissolved in 1 N sodium hydroxide (20 ml.), kept at 30°C in an ampoule sealed carefully with nitrogen. After ion exchange, the solution was titrated.

Measurement of UV-absorption with very thin cell.—Two quartz plates of the same size, with the side wall of the ordinary cell for Beckman spectrophotometer, was put together with picein as Fig. 8. The washing of the inside was effected by applying slight suction on one end, and immersing the other end in suitable solvent. The cell is very easily filled with solution by attaching a drop of the solution to one end of the dried cell, the solution being sucked into it automatically by capillary action. The thickness was measured by the absorption of methylene blue (316 mμ), methyl orange (458 mμ) and lignosulphonic acid (280 mμ), the average thickness being 0.136 ± 0.001 mm. Beckman spectrophotometer model DU was used.

Summary

α-Lignosulphonic acid has about one weak carboxyl group per 8–9 methoxyl, and about the same, or somewhat lesser amount of conductometrically titrable phenolic hydroxyl group, and both these groups correspond to the so-called weakly acidic group of lignosulphonic acid.

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