Studies on the Cooking Mechanism of Wood. XIII[1]. *On the Phenolic Hydroxyl Group of Lignosulphonic Acid*

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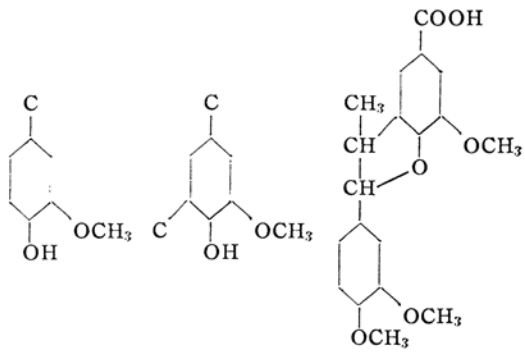
That the lignin in situ contains phenolic hydroxyl group was definitely established by the recent investigations of Richtzenhain[2]. By methylation of wood with diazomethane followed by permanganate oxidation, he could obtain veratric acid and isohemipinic acid. This fact proves that the lignin contains two types of phenolic hydroxyl groups, (I) and (II), already in wood. As it seems to be quite improbable that some destruction of the phenolic hydroxyl group occurs during the sulphonation, the phenolic hydroxyl groups already existed in wood must exist in lignosulphonic acid too.



Type (I) Type (II) (III)

A method to estimate the amount of the phenolic hydroxyl group of the lignin in wood was worked out, and the amount was estimated

1) Part XII, This Bulletin, 28, 653 (1955); cf. also short communication, ibid., 29, 209 (1956).
2) H. Richtzenhain, *Chem. Ber.*, 83, 488 (1950).

as 0.15–0.18/CH_3O. The amount of the phenolic hydroxyl group of the solid lignosulphonic acid, i.e. sulphonated lignin contained in the wood sulphonated at neutral pH, was also measured, and it was confirmed that the content was exactly the same as that of the lignin in situ. This fact proves that no new formation of phenolic hydroxyl group occurs during the sulphonation at neutral pH.

No definite conclusion has been obtained as yet, as to whether the sulphonation reaction accompanies the formation of phenolic hydroxyl group or not. Hägglund and Carlsson observed a new formation of hydroxyl group[3], and the nature of this hydroxyl group was thought by Freudenberg to be phenolic, formed by the opening of benzopyran or fran rings[4]. Hachihama, Shinra and Kyogoku recognized a quantitative relationship between the amount of sulphur introduced and the phenolic hydroxyl group formed[5]. Freudenberg, Lautsch and Piazolo, however, could not recognize any appreciable increase of phenolic hydroxyl group by sulphonation at low temperature, although the decrease of the amount of the ether oxygen was quite appreciable[6]. One of the reasons for such discrepancies may be due to the difference of the methods used for the estimation of the phenolic hydroxyl group.

The amount of the phenolic hydroxyl group of lignin itself depends also on the methods of estimation used. By two different methods, Freudenberg estimated the amount as one/3.9CH_3O[7] and one/1.7–3.3CH_3O[8]. Aulin-Erdtman introduced a spectroscopic method, and by the method she estimated the amount of phenolic hydroxyl group of lignosulphonic acid as one/4–6CH_3O. In our present communication, her spectroscopic method was used.

Low sulphonated lignosulphonic acid, obtained from the sulphonated wood by the Kullgren process[9], has according to Aulin-Erdtman 0.13 phenolic hydroxyl group per methoxyl group[10]. Our samples showed slightly greater values, but the difference was very little. This fact proves that no new formation of phenolic hydroxyl group occurs during the Kullgren process, either. It will also be concluded, from this fact that wood seems to contain no easily hydrolizable linkages, which can produce phenolic hydroxyl group. As the lignin in wood contains two types of phenolic hydroxyl groups, (I) and (II), phenolic hydroxyl groups of low sulphonated lignosulphonic acid belong also to these two types.

According to Aulin-Erdtman[10], ordinary lignosulphonic acid contains 0.17 phenolic hydroxyl group, 0.04 more than that of low sulphonated acid. As will be stated later, a slight increase of phenolic hydroxyl group was also recognized in the acidic further sulphonation of low sulphonated lignosulphonic acid, i.e. in the sulphonation of B-group region. Freudenberg showed previously, that the so-called Erdtman's acid (III) was sulphonatable by acidic sulphite solution, accompanying the formation of phenolic hydroxyl group by opening its coumaran structure[11]. This acid contains, however, carboxyl group in the para position to its benzyl-aryl ether bond belonging to phenyl-coumaran structure, which may affect the reactivity of the aryl ether bond. As will be stated later, dihydro-dehydro-diisoeugenol (XIV) was also found to be sulphonatable by acidic sulphite solution. Lindgren and Mikawa[12] confirmed that such structure reacts with thioglycolic acid very easily, whereby the phenyl-coumaran structure is split accompanying the new formation of phenolic hydroxyl group. Lignothioglycolic acid prepared from the completely methylated wood has about 0.16–0.2 phenolic hydroxyl group per methoxyl. This fact provides a possibility that the lignin in wood contains at most about this amount of phenyl-coumaran structure with benzyl-aryl ether linkage. From these experimental findings, it will reasonably be assumed, that such phenyl-coumaran structure exists in lignin, and a part of the B group must have such structure.

As stated previously, low sulphonated lignosulphonic acid contains two types of phenolic hydroxyl group, that of type (I) and (II). The sulphonation of B group accompanies the new formation of phenolic hydroxyl group, which is expected to belong to type (II), since a part of the B group may have phenyl-coumaran structure having benzyl-aryl ether bond. It will, therefore, be very interesting to know the amount of both these phenolic hydroxyl groups belonging to different types, in various lignin preparations. Conductometric titrations of many model compounds

3) E. Hägglund and G. Carlsson, *Biochem. Z.*, 257, 467 (1933).
4) K. Freudenberg, *Annual Rev. Biochem.*, 8, 81 (1939).
5) Y. Hachihama, H. Shinra and Y. Kyogoku, *J. Soc. Chem. Ind. Japan*, 47, 212 (1944).
6) K. Freudenberg, W. Lautsch and G. Piazolo, *Cellulosechem.*, 22, 97 (1944).
7) K. Freudenberg and H. Walch, *Ber.*, 76, 305 (1943).
8) K. Freudenberg, *Das Papier*, 1, 209 (1947); K. Freudenberg and D. Rasenack, *Ber.*, 86, 755 (1953).
9) C. Kullgren, *Svensk Kem. Tid.*, 44, 15 (1932).
10) G. Aulin-Erdtman, *Svensk Papperstidn.*, 55, 745 (1952); 56, 91 (1953).
11) K. Freudenberg, M. Meister and E. Flickinger, *Ber.*, 70, 500 (1937).
12) B. Lindgren and H. Mikawa, *Acta Chem. Scand.*, 8, 954 (1954).

showed that the phenolic hydroxyl group of type (I), i.e. that of the simple guaiacol type, was without exception titratable, that of type (II), however, was found to be conductometrically untitratable, even a slight change of inclination not being observed in the titration curve. This fact provides a very sharp method to measure tne frequency of both types of phenolic hydroxyl group in lignin. Aulin-Erdtman[10] reports that the model compounds having the phenolic hydroxyl group of type (II) are not neutralized completely even at about pH 12. She supposes the existence of some amount of such phenolic hydroxyl group (termed "hindered" phenolic hydroxyl group by Coggeshall[13].) in lignosulphonic acid.

By this method, it was found that low sulphonated lignosulphonic acid contains both types in approximately equal amounts. As the phenolic hydroxyl group of this acid is the same with that of the lignin in situ, the phenolic hydroxyl group of the lignin in wood may consist of about equal amounts of both phenolic hydroxyl groups. α-Lignosulphonic acid contains type (II) much more than type (I), the ratio being 7 : 3 in this acid. As a part of the B group is expected to be phenyl-coumaran structure, it is quite understandable, that type (II) increased very much after the sulphonation of the B group. The content of the type (I) is higher in birch α-lignosulphonic acid than in spruce α-acid, the ratio of type (I) and (II) being about 1 : 1. This fact will easily be understood, as the titrations of model compounds show that the phenolic hydroxyl group belonging to syringyl nucleus is conductometrically titratable, which can not form phenyl-coumaran structure.

On the Amount of Phenolic Hydroxyl Group and Phenyl-coumaran Structure of Lignin in Wood

As stated previously, Richtzenhain proved definitely that the lignin in situ contains already phenolic hydroxyl group. The amount, however, was not known. Based on the yield of veratric and isohemipinic acid, the frequency of the phenolic hydroxyl group is calculated to be one per 15.4 methoxyl group. This value is, however, only the lower limit of the frequency of the phenolic hydroxyl group, as one can not estimate the loss of these acids during the oxidation.

During the preparation of lignothioglycolic acid, the most reactive groups, i.e. X, Z and B, combine with thioglycolic acid[14,15] very quickly under comparatively mild conditions, thus protecting the reactive groups and preventing secondary reaction. It will, therefore, reasonably be assumed, that the phenolic hydroxyl group of lignothioglycolic acid is the sum of the phenolic hydroxyl group of lignin already existing in wood, and of that formed during the reaction with thioglycolic acid. The latter hydroxyl group may at least partly be formed from the phenyl-coumaran structure. It is, therefore, expected that the frequency of the phenolic hydroxyl group of lignothioglycolic acid, prepared from completely methylated wood, gives the upper limit of the frequency of the phenyl-coumaran structure of the lignin in situ. The difference of the amount of the phenolic hydroxyl group of the lignothioglycolic acid, prepared from untreated wood, and that prepared from the

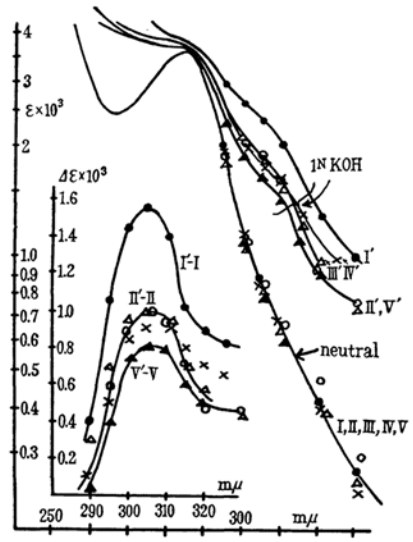


Fig. 1. UV-absorption spectra and $\Delta\varepsilon$-curves of lignothioglycolic acids prepared from various wood powders.

wood powders	CH_3O% of wood	CH_3O% of lignothioglycolic acid
(I) ● Spruce wood powder (s.)	—	11.81
(II) ○ CH_2N_2 methylated s.	11.91	13.88
(III) △ S. Sulphonated at neutral pH and then methylated with CH_2N_2	14.90	14.25
(IV) × S. methylated with Me_2SO_4	15.80	15.30
(V) ▲ 〃	22.10	16.15

13) N. Coggeshall, *J. Am. Chem. Soc.*, 69, 1620 (1947); N. Coggeshall and A. Gtessner, ibid., 71, 3150 (1949); 72, 2275 (1950). cf. also Kirk-Othmer, Encyclopedia of Chem. Tech., Vol. 10, 301 (1953).

14) H. Mikawa and K. Sato, *J. Chem. Soc. Japan Ind. Chem. Sec.*, 57, 605 (1954).

15) Part XI of this series. This Bulletin, 28, 649 (1955).

methylated wood is expected to be the same as the amount of the phenolic hydroxyl group of the lignin in situ.

Curves (I) and (I′) of Fig. 1 are the neutral and alkaline (1 N KOH) absorption spectra of the lignothioglycolic acid prepared from untreated wood powder, (II), (IV), (V) and (II′), (IV′), (V′) are those of the lignothioglycolic acids prepared from the methylated wood powder taken in neutral and alkaline media, respectively. In (I) and (I′) the molar extinction was calculated on the methoxyl basis, the positions of the curves (II)-(V) were, however, settled by shifting them so as to give the same extinction with the Curve (I) at 282 mμ maximum. By fixing the positions of the Curves (II)-(V) in this way, the positions of the other Curves (II′)-(V′) are also fixed. Curves (I)-(V) superpose each other almost completely over the whole range of wave-lengths. So-called $\Delta\varepsilon$-curves obtained from these neutral and alkaline spectra are shown in the same figure. (I′)-(I) is the value obtained for the lignothioglycolic acid prepared from the untreated wood powder, (II′)-(II) is from the diazomethylated wood powder (CH_3O 11.9%). In order to comfirm, whether the methylation with diazomethane is complete or not, wood powders methylated with dimethyl sulphate up to CH_3O 15.80 and 22.10% were also investigated. The curve obtained for the latter is (V′)-(V). The difference of (I′)-(I)=1550 and (V′)-(V)=800, i.e. 750 corresponds to the amount of the phenolic hydroxyl group of the lignin in wood, the amount being 0.18-0.15/CH_3O by assuming the $\Delta\varepsilon$ value for monophenols as 4000-5000, according to Aulin Erdtman.

As seen in the figure, the amount of the phenolic hydroxyl group of the lignothioglycolic acid prepared from diazomethylated wood and from the wood sulphonated at neutral pH followed by diazomethylation (Curves (III) and (III′)) is approximately the same, which fact proves that no new phenolic hydroxyl group was formed during the sulphonation at neutral pH. The phenolic hydroxyl group corresponding to (V′)-(V), i.e. $\Delta\varepsilon$=800 or one per 5-6.3 CH_3O=0.16-0.2/CH_3O, is that formed during the reaction with thioglycolic acid, and this amount is expected to be the upper limit of the amount of the phenyl-coumaran structure in lignin.

On the Increase of Phenolic Hydroxyl Group of Low Sulphonated Lignosulphonic Acid by its Further Sulphonation

In a previous communication[15], further sulphonation of low sulphonated lignosulphonic acid was studied. The amount of the phenolic hydroxyl group of many sulphonic acids prepared at that time was measured by spectroscopic method, and the values thus obtained were plotted against the time of the sulphonation (Fig. 2). In this figure,

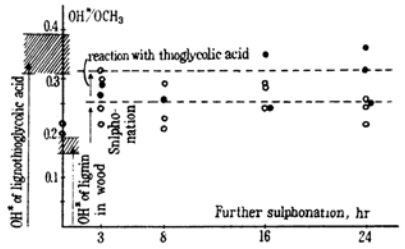


Fig. 2. Amount of the phenolic hydroxyl group of low sulphonated lignosulphonic acid (LSLSA) (○), LSA obtained by acidic further sulphonation of LSLSA (○) and of these acids after the reaction with thioglycolic acid (●). $\Delta\varepsilon$ value of monophenols was assumed to be 4000.

lignosulphonic acid corresponding to time zero is the low sulphonated lignosulphonic acid used. As stated previously, the amount of the phenolic hydroxyl group of this acid is approximately the same as that of the lignin in situ.

As can be seen in the figure, the content of the phenolic hydroxyl group increases about 0.1/CH_3O by further sulphonation. As stated previously, this newly formed phenolic hydroxyl group may be of type (II) formed by the opening of the phenyl-coumaran structure. As low sulphonated lignosulphonic acid contains phenolic hydroxyl groups belonging to type (I) and type (II) in equal ratio with the lignin in situ, the content of the type (II) must be higher in α-lignosulphonic acid. It will, therefore, be very interesting to measure the ratio quantitatively.

Conductometric Titrations of Model Compounds and the Method of the Estimation of Both Type (I) and Type (II) Phenolic Hydroxyl Group

In a previous communication[15], it was shown that the conductometrically observable so-called weakly acidic group of lignosulphonic acid consists of weak carboxyl group and the "conductometrically titratable" phenolic hydroxyl group. As an example, the curves of the conductometric titration of low sulphonated lignosulphonic acid are shown in Fig. 3. With extremely thin cell, UV-absorption spectra were taken at points A, B, C, D and E of the conductivity curve by using the

16) Part XII of this series, *loc. cit.*

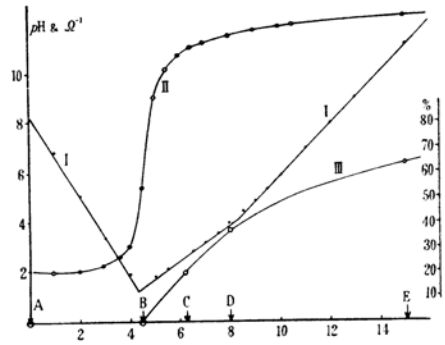


Fig. 3. Conductometric titration (I) and potentiometric titration (II) of low sulphonated lignosulphonic acid, and the percentage of the ionized phenolic hydroxyl group measured during the titration (III).

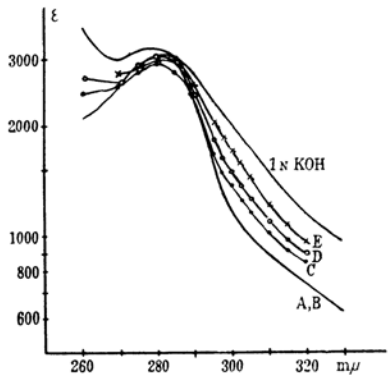


Fig. 4. UV-absorption spectra taken at points A-E of Fig. 3.

same technique as mentioned in the previous communication. (Fig. 4). The differences of the spectra taken at B-E, and in 1 N KOH, and the spectrum taken at A were indicated in Fig. 5. The percentage of the ionized

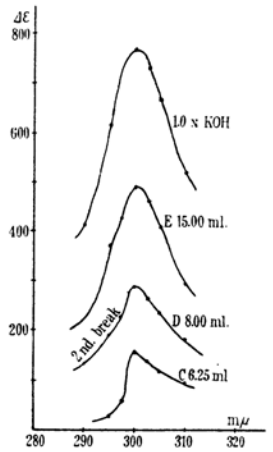


Fig. 5. $\Delta\varepsilon$-curves obtained at points C~E of the conductometric titration curve of the low sulphonated lignosulphonic acid shown in Fig. 3.

phenolic hydroxyl group at various stages of the titration calculated from Fig. 5 is shown by Curve (III) of Fig. 3. As can be seen, the phenolic hydroxyl group, which remains unionized before the second break, amounts to approximately 55% of the total phenolic hydroxyl group.

As discussed in the previous papers, simple

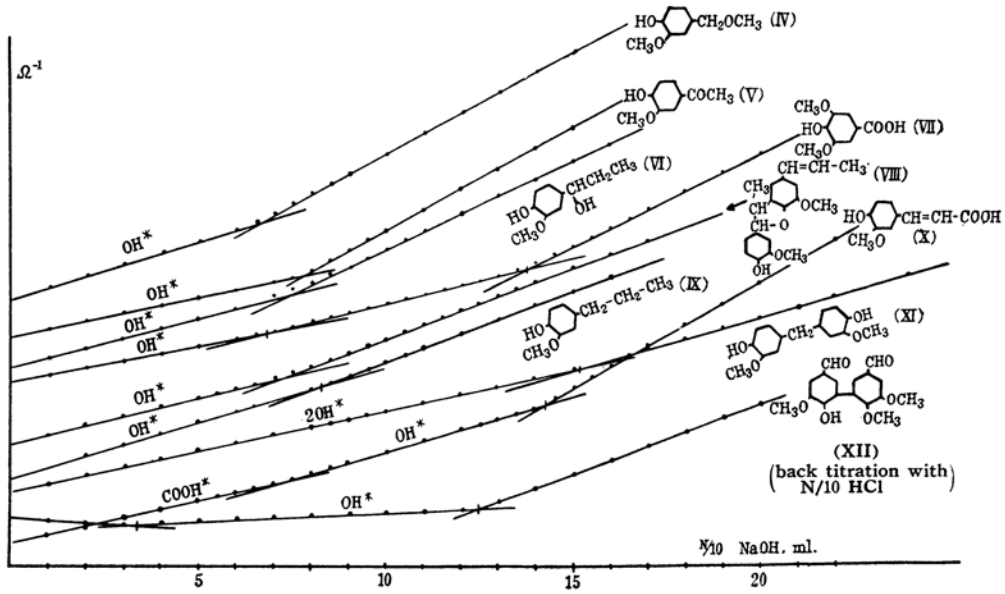


Fig. 6. Conductometric titrations of various model compounds in 30~50% aqueous alcohol. (Almost quantitative values are obtained in every case)

guaiacol type phenolic hydroxyl group was expected to be titratable. In order to confirm it, many model compounds were titrated conductometrically in aqueous alcohol (30–50%). As can be seen in Fig. 6, all these compound were titrated quantitatively without exception. As it is known that pK values of phenols are larger in alcohol than in water[17], guaiacol type phenolic hydroxyl group must be titratable in aqueous solution too, as they are titrable in aqueous alcohol. As an example of a water soluble model, vanillyl sulphonic acid was titrated in the previous communication. Another water soluble compond. guaiacyl glycerol (XVII) was titrated (Fig. 7),

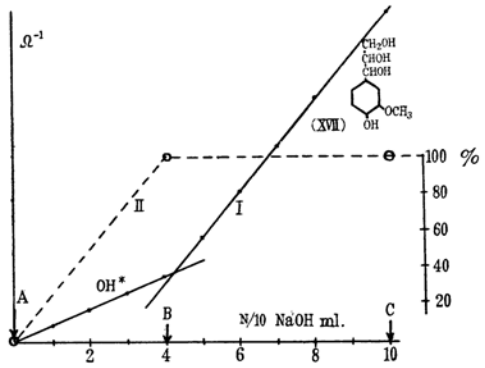


Fig. 7. Conductometric titration (I) of guaiacyl glycerol and the percentage of the ionized phenolic hydroxyl group measured at points A∼C (II).

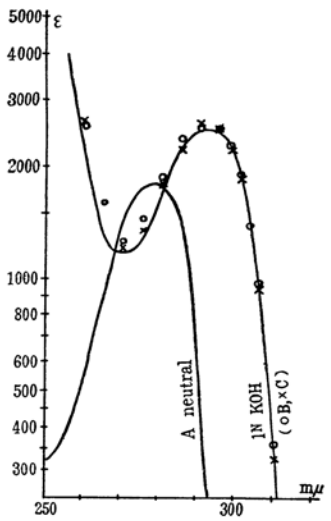
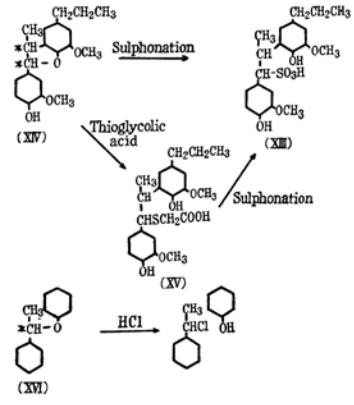


Fig. 8. Change of the UV-absorption spectrum during the titration of guaiacyl glycerol shown in Fig. 7.

As the titration proceeds along the Curve (I), the phenolic hydroxyl group ionized along the Curve II and at point B, i.e. at the end point of the titration, the ionization of the phenolic hydroxyl group was spectroscopically complete (Fig. 8). Based on these experimental findings, it will reasonably be concluded, that at the end point of the conductometric titration of the "conductometrically titratable" phenolic hydroxyl group, this group must be completely in phenolate form, i.e. that the conductometric titration and the ionization of the phenolic hydroxyl group proceeds pararell in equal amounts.

As an example of the phenol belonging to type (II), a model compound (XIII) was titrated.

This compound was synthesized by sulphonating racemic dihydro-dehydro-diisoeugenol (XIV) or its thioglycolic acid adduct (XV) with acidic sulphite solution. (XIII) was obtained in crystalline form as its benzylthiuronium salt having a sharp melting point. The structure of this compound was concluded from the analyses and its UV-absorption spectra, taken in acidic and in alkaline media shown in Fig. 10. As dihydro-dehydro-diisoeugenol contains two asymmetric carbon atoms, the product is expected to be a mixture of two different racemic modifications, provided that the racemization at the α-carbon atom is involved in the reaction. As the product was obtained, however, in crystalline form, having a sharp melting point, it appears that the compound isolated may be one of the two expected racemic modifications, if the reaction involves racemization at the α-carbon atom. It may, however, also be possible that the reaction proceeds under complete retention or complete inversion of the benzylaryl ether bond resulting in a formation of only one racemic modification. In connection with this problem, it may be remarked that Hart[18] reports that the configuration of α-phenoxy ethylbenzene (XVI) is not altered when its benzylaryl ether bond is split by hydrogen chloride.



As can be seen from the Curve (I) of Fig. 9, the amount of the conductometrically titratable

17) W. Treadwell and G. Schwarzenbach, *Helv. Chim. Acta*, **11**, 386 (1928).

18) H. Hart and H. Eleuterio, *J. Am. Chem. Soc.*, **76**, 1379 (1954).

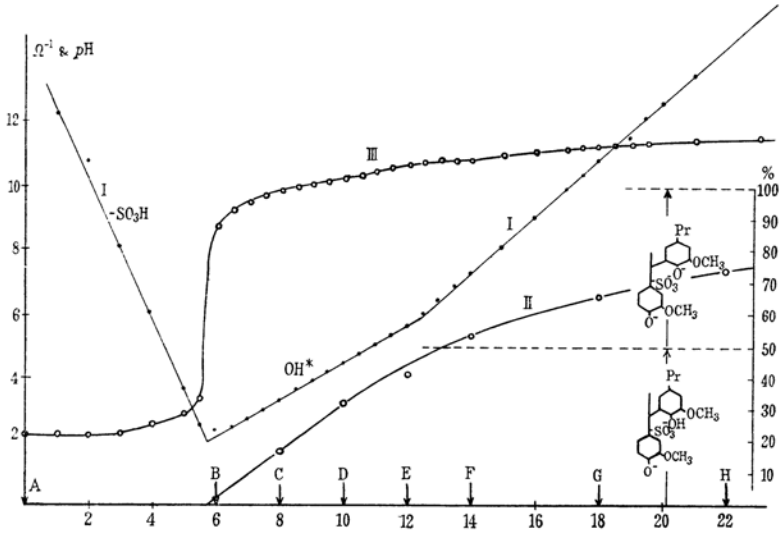


Fig. 9. Conductometric (I) and potentiometric (III) titrations of the model compound (XIII) and the percentage of the phenolic hydroxyl group ionized during the titration.

phenolic hydroxyl group is equivalent to the amount of the sulphonic acid group, i.e. only one phenolic hydroxyl group is conductometrically titrable, which is expected to be a simple guaiacol type. Curve (II), which indicates the ionization of the phenolic hydroxyl group during the titration, shows that only 50% of the total phenolic hydroxyl group is ionized at the second break of the titration curve. Even after the second break, the ionization of the remaining phenolic hydroxyl group proceeds only gradually; no quantitative relation exists, however, between the added alkali and the increase of the ionization, the phenolic hydroxyl group titrated in this region being too weak and the hydrolysis of the phenolate ion being consequently too great. Even a slight change of inclination was not observed in the titration Curve (I) around the expected third break, 18 ml. region. UV-absorption curves measured at A-H and the corresponding $\Delta\varepsilon$ curves are shown in Fig. 10 and 11 respectively.

From these experimental findings, it will be possible to conclude as follows. Potentiometric titration cannot differentiate the phenolic hydroxyl group of type (I) and (II). The curve of the spectroscopically determined percentage of the ionized phenolic hydroxyl group against the volume of the alkali added, i.e. for example Curve (II) of Fig. 9, does not show any distinct break between the two types of the phenolic hydroxyl groups. Although type (I) is conductometrically titratable and type (II) untitratable, it is impossible to determine the amount of both types by conductometric titration alone, as the phenolic

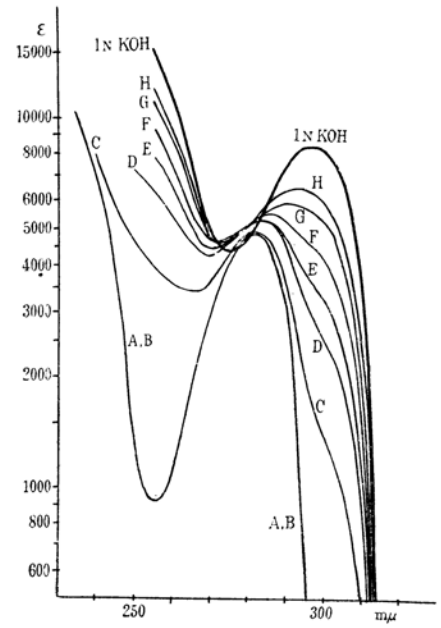


Fig. 10. Change of the UV-absorption spectrum observed during the titration of the compound (XIII) shown in Fig .9.

hydroxyl group of type (I) can not be distinguished by conductometric titration from the weak carboxyl group present in lignosulphonic acid. By combining conductometric titration (Curve I) and the curve of the percentage of the ionized phenolic hydroxyl group (Curve II), one can determine very clearly the amount of both types separately, the amount of the phenolic hydroxyl group ionized before the second break being equal

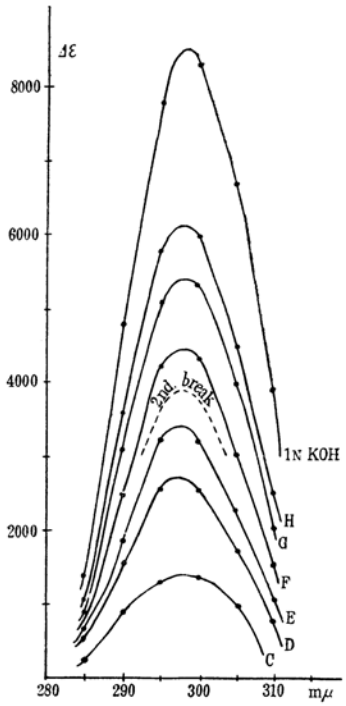


Fig. 11. $\Delta\varepsilon$-curves obtained at points C~H of the conductometric titration curve of the compound (XIII) shown in Fig. 9 and 10.

to that of type (I) and the remaining one being that of type (II).

Ratio of the Phenolic Hydroxyl Group belonging to Type (I) and Type (II) in various Lignosulphonic Acid Preparations

Fig. 3 shows the conductometric titration of the low sulphonated lignosulphonic acid and, as stated previously, about 40–50% of the total phenolic hydroxyl group was found to be conductometrically titratable and 60–50% remained untitrated in this case. The former may be of type (I) and the latter type (II). As the phenolic hydroxyl group of the lignin in wood may be the same as that of the low sulphonated lignosulphonic acid, it appears that the ratio of the phenolic hydroxyl group of the lignin in wood belonging to type (I) and (II) may be the same as that of the low sulphonated lignosulphonic acid, i.e. the amounts of these two types are thought to be about the same in this case, too.

Titration curves of an α-lignosulphonic acid was shown by Fig. 3 of the previous communication (Part XII). Only about 30% of the total phenolic hydroxyl group was conductometrically titratable. The amount of the phenolic hydroxyl group of type (II) must be, therefore, much higher in this acid than in low sulphonated lignosulphonic acid or the lignin in situ. As stated previously, the increase of the amount of type (II) may be attributed to the sulphonation of phenyl-coumaran structure in the sulphonation of B-group region.

Conductometric titration and the change of the UV-spectrum of the birch α-lignosulphonic acid are shown in Fig. 12 and 13.

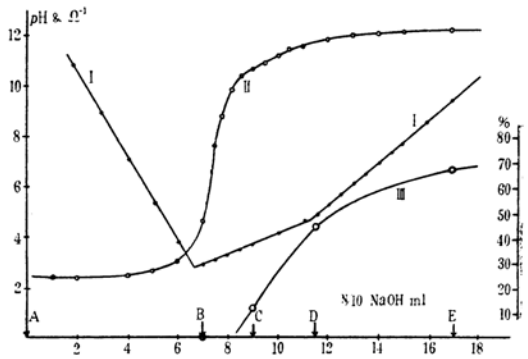


Fig. 12. Conductometric (I) and potentiometric titrations (II) of birch α-lignosulphonic acid, and the percentage of the phenolic hydroxyl group ionized during the titration (III).

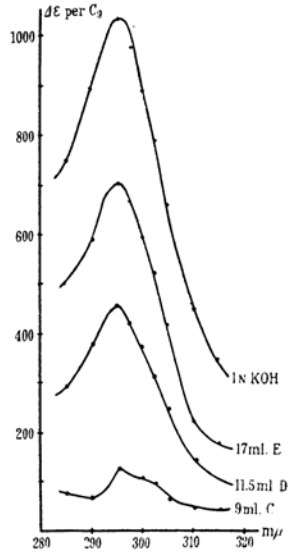


Fig. 13. $\Delta\varepsilon$-curves at points C~E of the titration curve of birch α-lignosulphonic acid shown in Fig. 12.

Conductometrically titratable phenolic hydroxyl group is about 50% of the total group in this case. The comparatively higher content of type (I) in this acid may be attributed to the existence of syringyl nucleus, which cannot form phenyl-coumaran structure. That the phenolic hydroxyl group belonging to syringyl

nucleus is conductometrically titratable was confirmed by the titration of syringic acid shown in Fig. 6.

Experimental

Methylation of various Wood Powders.—Methylation of wood powder with dimethyl sulphate was performed as usual with concentrated alkali at room temperature. Methylation with diazomethane was performed by simply keeping wood powder in etherial diazometane solution for about a week, changing the solution several times with a fresh one. Sulphonated wood powder was prepared by sulphonating at pH 6 for ten hours at 135°. Analyses of the methylated wood powders are shown in Fig. 1.

Preparation of Lignothioglycolic Acid from These Methylated Wood Powders.—To the methylated wood powder (5 g.) were added fresh distilled thioglycolic acid (25 g.) and 2N HCl (2.5 ml.), and the mixture was heated at 100° for two hours. A large amount of water was added, and the precipitate separated and washed with water by centrifuge. The residue was kept in 0.5N NaOH (50 ml.) over-night, the carbohydrate which remained insoluble was separated, and the lignothioglycolic acid was precipitated by dilute hydrochloric acid and centrifuged, washed with water, dissolved in a little amount of acetone, centrifuged and a mixture of alcohol and ether was added to the clear acetone solution of the lignothioglycolic acid. The reprecipitated lignin was washed with alcohol-ether, ether and petroleum ether successively. The yield of the cream colored powder thus obtained was 0.5–0.7 g. in every case. Analytical values are shown in Fig. 1.

Measurement of the UV-Absorption Spectra of Various Lignothioglycolic Acids.—Lignothioglycolic acid (ca. 10 mg.) was dissolved in dioxane (0.5 ml.) containing several drops of water. The solution was made up to 30 ml. with absolute alcohol purified with NaOH and zinc dust. When the spectrum in neutral medium is to be measured, 4 ml. of this solution was diluted with the same purified alcohol to 30 ml., and the alkaline spectrum was measured with the solution made by diluting 4 ml. of the solution with 60% aqueous alcohol and 3 ml. of 10N KOH, to 30 ml. The results were shown in Fig. 1.

Conductometric Titrations of Lignosulphonic Acids.—The method was the same as in the preceding papers, Part (XI) and (XII). 500 mg. of barium lignosulphonate was dissolved in 20 ml. of water, passed through cation exchanger IR 120 and the eluate was made up to 50 ml. The solution was titrated conductometrically with 0.1N sodium hydroxide solution.

Syntheses of Known Model Compounds.—Vanillyl methyl ether (IV): B. Leopold, *Svensk Papperstid.*, **55**, 816 (1952); acetovanillone (V): K. Nakazawa, *J. Pharm. Soc. Japan*, **74**, 836 (1954); α-guaiacyl propanol (VI): $LiAlH_4$ reduction of propioguaiacone acetate synthesized according to Nakazawa, loc. cit.; syringic acid (VII): M. Bogert and B. Coyen, *J. Am. Chem. Soc.*, **51** 569 (1929); Dehydro-diisoeugenol (VIII): B. Leopold, *Acta Chem. Scand.*, **4** 1523 (1950); coeruligno! (IX): hydrogenation of isoeugenol with Pd-C; ferulic acid (X); Adams, Organic Reactions Vol. I, p. 250; 3, 3′-dimethoxy-4, 4′-dihydroxy-diphenyl methane (XI): H. Mikawa, *Bull. Chem. Soc. Japan*, **27**, 53 (1954); guaiacyl glycerol (XVII): E. Adler and S. Yllner, *Acta Chem. Scand.*, **7**, 570 (1953).

Synthesis of Dehydro-divanillin Monomethyl Ether (XII).—Dehydro-divanillin[19] (25 g.) was dissolved in a sodium hydroxide solution, dimethyl sulphate (30 g.) added and the methylation was performed at room temperature. Dimethyl ether separated was filtered and the filtrate was acidified with carbon dioxide. A mixture of monomethyl ether and the starting material was washed with methanol and extracted with hot benzene. The monomethyl ether thus extracted was recrystallized from benzene, m.p. 196.5–197°, yield 4.5 g.

Anal. Found: C, 64.44; H, 5.30; CH_3O, 29.5. Calcd. for $C_{17}H_{18}O_6$: C, 64.55; H, 5.10; CH_3O, 29.4%.

Synthesis and Conductometric Titration of α-(3-Methoxy-4-hydroxyphenyl)-β-(2-hydroxy-3-methoxy-5-propylphenyl)-*n*-propane Sulphonic Acid (XIII).—*Method I:* Dehydro-diisoeugenol (racemate) was hydrogenated with Pd-C to dihydrodehydro-diisoeugenol. To 4.7 g. of Di-De-Di was added 50 ml. of cooking acid (17 g. of NaOH and 50 g. of SO_2 in one liter of 50% alcohol) and the mixture was heated in a quickly rotating autoklave at 140° for twenty hours. A slight excess of sulphuric acid was added, SO_2 expelled in vacuo, and the solution was neutralized with $BaCO_3$, centrifuged, and concentrated to about 30 ml. Benzylthiuronium salt of the sulphonic acid was precipitated by adding conc. solution of benzylthiuronium hydrochloride, washed well with water, dissolved in a small amount of alcohol, filtered and reprecipitated with water. The precipitate separated at first as oil, solidified over-night. This was purified in the same way until constant m.p. was reached. M.p. 136–138°, 0.8 g. After being kept at 80° in vacuo with P_2O_5 for two days the m.p. was 145–147°.

Anal. Found: C, 58.43; H, 6.17; N, 4.98; CH_3O, 11.6. Calcd. for $C_{28}H_{33}O_7N_2S_2$ (benzylthiuronium salt of XIII): C, 58.3; H, 6.24; N, 4.86; CH_3O, 10.75%.

99.6% of the sulphonic acid group of this compound was titrated conductometrically.

Method II: 4 g. of Di-De-Di was reacted with thioglycolic acid[12] and the product XV was treated as in method I. Treating the product in the same way as above, 0.5 g. of the benzylthiuronium salt melting at 145–147° was obtained. Mixed with the product obtained by Method I, no melting point depression was observed. 0.8 g. of dihydrodehydro-diisoeugenol was recovered, which fact shows that a part of the thioglycolic acid adduct splits off its thioglycolic acid residue, regenerating the phenyl-coumaran ring.

Conductometric titration of (XIII): 400 mg. of the benzylthiuronium salt was dissolved in 10 ml. of alcohol, 20 ml. of water added and warmed. The warm solution was passed through a column

19) K. Elbs and H. Lerch, *J. prak. Chem.*, 93, 1 (1916).

of ion exchange resin IR 120, washed with warm aqueous alcohol until neutral pH. Alcohol was boiled off in vacuo and the solution was diluted with water to 50 ml. and conductometrically titrated.

Summary

The amount of the phenolic hydroxyl group of the lignin in situ was estimated to be about one per 5–6 methoxyl. Phenolic hydroxyl group of low sulphonated lignosulphonic acid is the same as that of the lignin in situ. There exist two types of phenolic hydroxyl groups (I) and (II) in lignin and lignosulphonic acid, the former being conductometrically titratable and the latter untitratable. With several lignosulphonic acid preparations, the ratios of these two types of phenolic hydroxyl groups were measured, the ratio being 1 : 1 with lignin in wood, low sulphonated lignosulphonic acid, and birch α-lignosulphonic acid and about 3 : 7 with α-acid of gymnosperm origin. The structures of these two types of phenolic hydroxyl groups were suggested.

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