On the Cooking Mechanism of Wood. XVII. Further Investigations on the Conductometric Titrations of Lignin Models with Phenolic Hydroxyl Groups and a Brief Theory of the Conductometric Titration of Phenols

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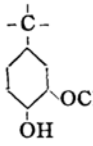
(Received March 4, 1958)

Conductometrically Untitratable *o*-Substituted Phenolic Hydroxyl Group.— In part XIII of this series[1], it was reported that although simple guaiacol-type phenolic hydroxyl group (I) was conductometrically titratable, having a very clear "break" (the neutralization point), non-guaiacyl phenolic hydroxyl group of the model sulfonic acid (III) was conductometrically untitratable. Assuming in general that the phenolic hydroxyl groups belonging to type-II are conductometrically untitratable, a method of the separate estimation of both type-I and -II phenolic hydroxyl groups of lignosulfonic acid was wroked out with the aid of the ultraviolet absorption spectra taken simultaneously with the conductometric titration. It seems, therefore, to be quite important to make further confirmation of the non-titratability of such phenolic hydroxyl group, with other model compounds.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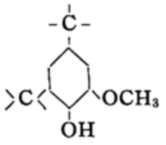
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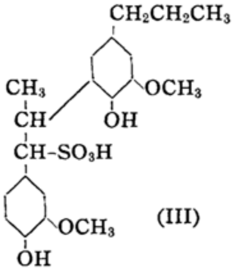
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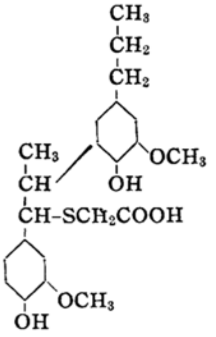
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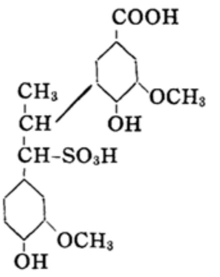
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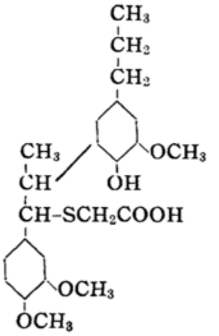
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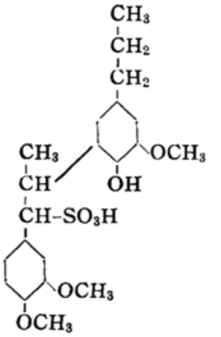
(VII)

Four model compounds IV-VII, all containing type-II phenolic hydroxyl groups, were therefore conductometrically titrated and it was confirmed that such phenolic hydroxyl groups were not conductometrically titratable.

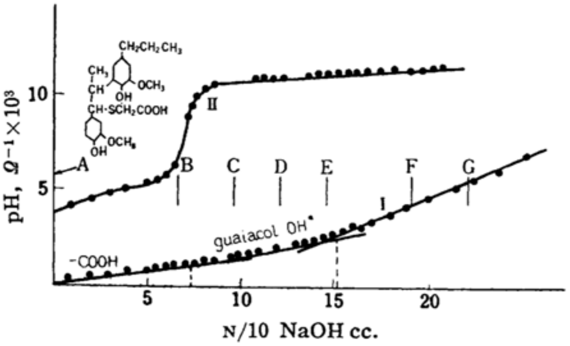

Fig. 1. Conductometric(I) and potentiometric(II) titrations of the model compound IV.

As shown in Figs.1—3, conductometrically titratable groups of the model compound IV are its carboxyl group and one of its two phenolic hydroxyl groups, one phenolic hydroxyl, possibly that of type II, remaining untitrated.

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[1] H. Mikawa, K. Sato, C. Takasaki and K. Ebisawa, This Bulletin **29**, 245 (1956).

Fig. 4 shows that the titratable groups of the model compound V are as expected the sulfonic acid group, the carboxyl group and only one of its two phenolic hydroxyl groups, the ratio of the strongly acidic part and the weakly acidic part of the titration curve being 1:2. No perceptible "break" existed in the weakly

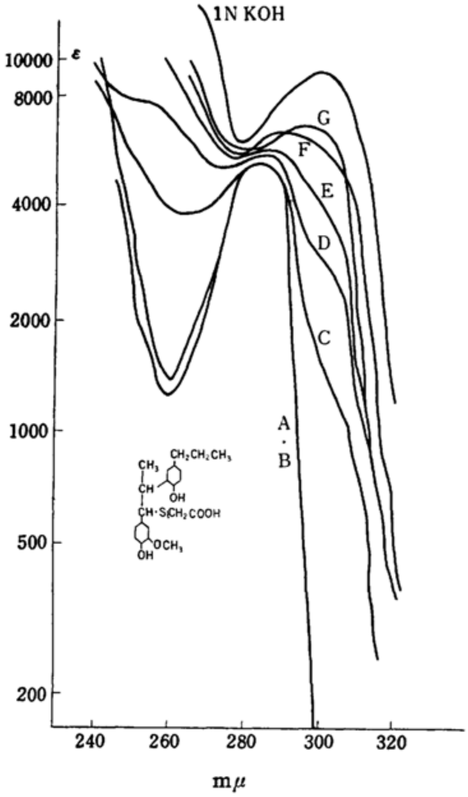


Fig. 2. Change of the UV-absorption spectrum observed during the titration of the compound IV.

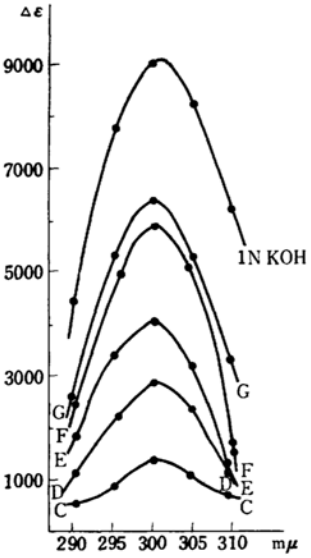


Fig. 3. Δε-curves obtained at point C—G of the conductmetric titration curve of the compound IV shown in Figs. 1 and 2.

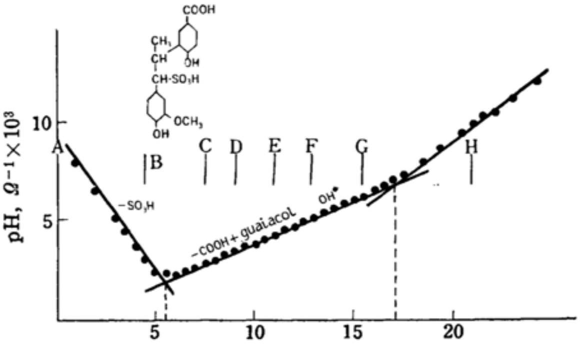


Fig. 4. Conductmetric titration curve of model compound V.

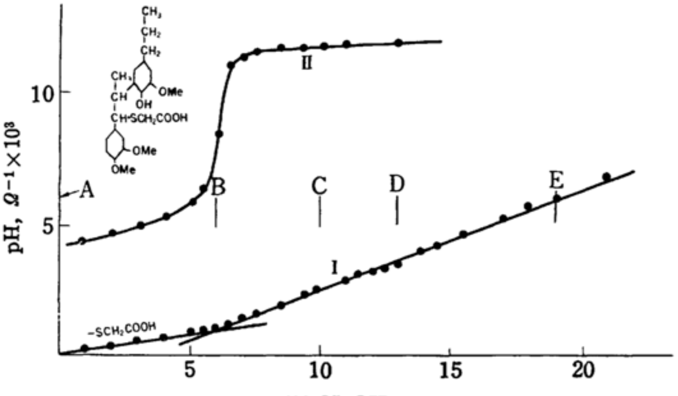


Fig. 5. Conductmetric (I) and potentiometric (II) titrations of the model compound VI.

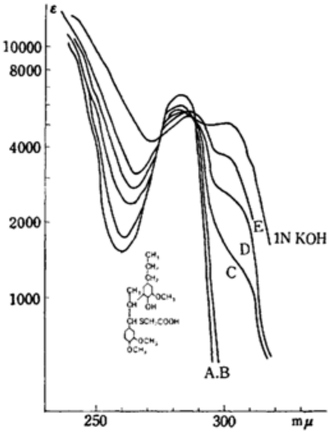


Fig. 6. Change of the UV-absorption spectrum observed during the titration of the compound VI.

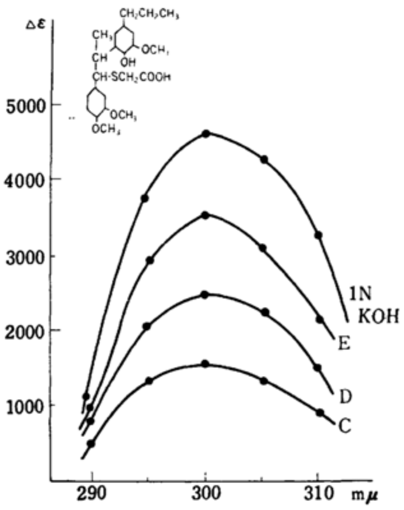


Fig. 7. $\Delta\varepsilon$-curves obtained at point C～E of the conductometric titration curve of the compound VI shown in Figs. 5 and 6.

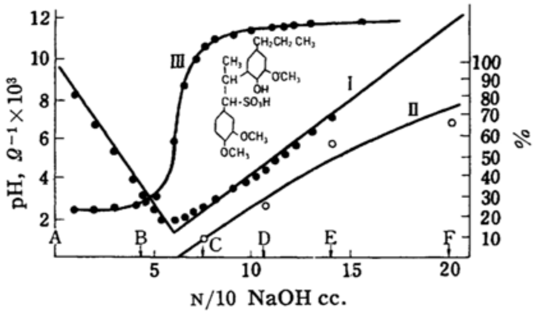


Fig. 8. Conductometric (I) and potentiometric (III) titrations of the model compound VII and the percentage of the phenolic hydroxyl group ionized during the titration (II).

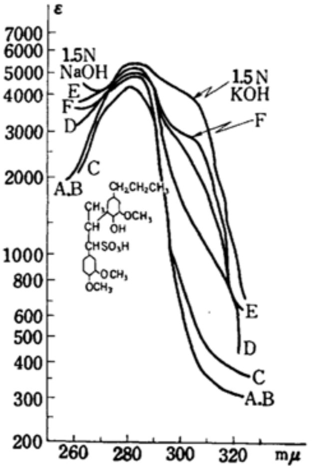


Fig. 9. Change of the UV-absorption curve observed during the titration of the compound VII shown in Fig. 8.

acidic part just as in the case of lignosulfonic acid. Thus, the separation of carboxyl group and the conductometrically-titratable phenolic hydroxyl group seems to be impossible even in the case of the model compound.

Model compound VI demonstrates, as shown in Figs. 5—7, most clearly that type-II phenolic hydroxyl group is not conductometrically titratable. The titratable group is only its carboxyl group in this case, type-II phenolic hydroxyl of this compound having no effect on the titration curve.

The same is true again in the case of the model compound VII, as shown in Figs. 8—9. Type-II phenolic hydroxyl of this compound was not titrated.

From the above findings it will now safely be concluded that type-II phenolic hydroxyl group of at least III-VII type may be in general definitely conductometrically untitratable. A method of the separate estimation of both type I and type II phenolic hydroxyl groups, worked out in the previous communication, may therefore be valid in general.

Conductometric Titration of *o, o′*-Diphenol-Type Phenolic Hydroxyl Groups.—We have now considerable accumulation of the facts supporting the existence of *o, o′*-diphenol type phenolic hydroxyl groups in lignin. Among others according to the recent view of the biosynthesis of lignin, the formation of such *o, o′*-diphenol type linkage is expected during the dehydrogenative condensation of coniferyl alcohol or other monomeric phenolic lignin precursors²⁾, as the phenols, without double bond conjugated with benzene nucleus in its para position, dimerize easily resulting in the formation of *o, o'*-diphenol structure by dehydrogenation³⁾. The results of the nitrobenzene oxidation of lignin and lignin-model compounds support also the existence of such structure in lignin, as degradation products having such *o, o'*-diphenol-type linkage are obtained only from lignin but not from model compounds with simple guaiacol type nucleus⁴,⁵⁾.

Three water-soluble model compounds VIII—X were prepared and titrated conductometrically and the results are summarized in Fig. 10.

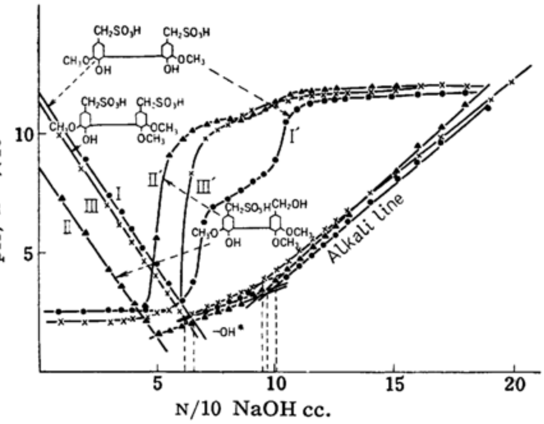
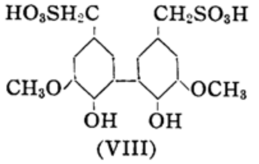
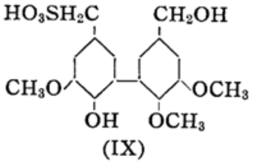


Fig. 10. Conductometric and potentiometric titrations of the model compounds VIII—X.

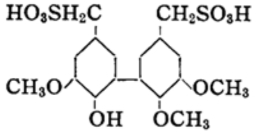
Only one of the two phenolic hydroxyl groups of the compound VIII was found to be titratable as shown by curves I and I' of the same figure. Phenolic hydroxyl groups of the compounds IX and X were conductometrically titratable (cf. curves II, II'; III and III'). That the phenolic hydroxyl group of the compound XI was conductometrically titratable by back titration in aqueous alcohol solution, as it was already reported in part XIII of this series¹⁾.



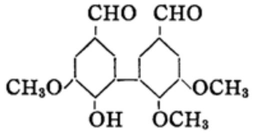
(VIII)



(IX)



(X)



(XI)

According to G. Aulin-Erdtman one of the phenolic hydroxyl groups, which belong to *o, o'*-diphenol is very strongs, on the other hand, the remaining one is extremely weak⁶⁾. It has been assumed that, owing to the formation of hydrogen bonding between two hydroxyl groups, a proton belonging to any one of these two hydroxyl groups acquires very strong tendency for ionization, although the remaining one is held firmly by net negative charge left after the ionization of one phenolic hydroxyl group, resulting in weakening of the acidity of this second hydroxyl group. As the phenolic hydroxyl groups of monomethyl ethers IX—XI are conductometrically titratable, there seems to exist no strong hydrogen bonding between phenolic hydroxyl group and methoxyl group in these structures.

We shall now be able to summarize the limitations of our method of the separate estimation of type-I and II phenolic hydroxyl groups as follows. If lignosulfonic acid contains *o, o'*-diphenol type structure or its monoether structure like those of VIII—XI, (i) one phenolic hydroxyl group may be estimated per such structure as conductometrically titratable type-I hydroxyl group; (ii) one very weak phenolic hydroxyl group of *o, o'*-diphenol structure will be missed completely in so far as the total amount of phenolic hydroxyl groups is estimated spectroscopically. The type-I phenolic hydroxyl group estimated by our method may, therefore, contain half of the phenolic hydroxyl groups belonging to *o, o'*-diphenol structure and that belonging to *o, o'*-diphenol monoether structure if any.

Brief Theory of the Conductometric Titration of Very Weak Phenols.—As stated above, the behavior of type-I and II phenolic hydroxyl groups in conductometric titration is very different, the former being titratable while the latter is completely untitratable. As it is easily expected that the difference between the two types of phenols is due to the difference of dissociation constants of both types of phenolic hydroxyl groups, it

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2) K. Freudenberg and Hubner, *Chem. Ber.*, **85**, 1181 (1952).
K. Freudenberg and H. Dietrich, ibid, **86**, 4 (1953).
K. Freudenberg and W. Fuche, ibid., **87**, 1824(1954).

3) H. Erdtman, *Biochem. Z.*, **258**, 172 (1933).

4) I. A. Pearl, *J. Am. Chem. Soc.*, **72**, 2309 (1950).

5) J. C. Pew, ibid., **77**, 2831 (1955).

6) G. Aulin-Erdtman, *Svensk Papperstid.*, **57**, 745 (1954).

must be interesting to make a brief theoretical discussion on the conductometric titration of phenols having different dissociation constants.

Assume that a strong base BOH is added to a solution of a weak acid (phenol) HA of concentration [S] and the total volume of the solution remains constant. Applying the mass law to the dissociation of the acid:

$$[\mathrm{H}^+]=K_a[\mathrm{HA}]/[\mathrm{A}^-] \qquad (1)$$

where K_a is the dissociation constant of the acid HA. From the principle of electroneutrality of the solution it follows that:

$$[\mathrm{A}^-]+[\mathrm{OH}^-]=[\mathrm{B}^+]+[\mathrm{H}^+] \qquad (2)$$

Since the total amount of the acid HA used is [S]:

$$[\mathrm{HA}]=[\mathrm{S}]-[\mathrm{A}^-] \qquad (3)$$

Substituting 2 and 3 into 1 to eliminate both $[\mathrm{A}^-]$ and [HA], one finds that:

$$[\mathrm{H}^+]=K_a\frac{1-[\alpha_t+([\mathrm{H}^+]-[\mathrm{OH}^-])/[\mathrm{S}]]}{\alpha_t+([\mathrm{H}^+]-[\mathrm{OH}^-])/[\mathrm{S}]} \qquad (4)$$

where $\alpha_t=[\mathrm{B}^+]/[\mathrm{S}]$ represents the ratio of the amount of the added base BOH to the total amount of the acid. Since the pH of the solution is in alkaline side throughout the titration, the hydrogen ion concentration is negligibly small in comparison to that of hydroxyl ion:

$$[\mathrm{H}^+]\ll[\mathrm{OH}^-]$$

Hence from equation 4 it follows that:

$$[\mathrm{H}^+]=K_a\left[1-\alpha_t+\frac{[\mathrm{OH}^-]}{[\mathrm{S}]}\right]\Big/\left[\alpha_t-\frac{[\mathrm{OH}^-]}{[\mathrm{S}]}\right] \qquad (5)$$

Eliminating $[\mathrm{H}^+]$ by using ion-product of water $K_w=[\mathrm{H}^+][\mathrm{OH}^-]$, $[\mathrm{OH}^-]$ can be calculated:

$$[\mathrm{OH}^-]=-\frac{1}{2}\left[\left([\mathrm{S}]-[\mathrm{S}]\alpha_t-\frac{K_w}{K_a}\right)+\sqrt{\left([\mathrm{S}]-[\mathrm{S}]\alpha_t-\frac{K_w}{K_a}\right)^2-4\frac{K_w}{K_a}[\mathrm{S}]\alpha_t}\right]$$

This equation gives the concentration of hydroxide ion $[\mathrm{OH}^-]$ of the solution of weak acid HA of concentration [S] when titrated with strong base BOH until α_t of the equivalent point. When the concentration [S] is assumed to be 0.01 normal, the concentration of the hydroxide ion increases during the titration for phenols having different pK values 9 to 12, as shown in Fig. 11.

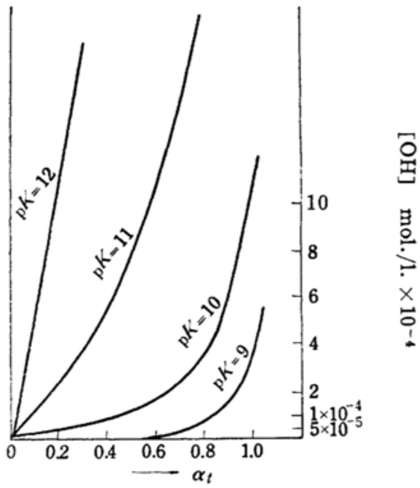

Fig. 11. The increase of the concentration of the hydroxide ion during the titration of phenols having various pK values.

Next, the specific conductivity of this solution is the summation of the products of the mobilities and one thousandth of the concentrations of the ions, as the concentration is expressed by mol./liter, that is

$$\kappa\cdot10^3=L_{\mathrm{H}^+}[\mathrm{H}^+]+L_{\mathrm{OH}^-}[\mathrm{OH}^-]+L_{\mathrm{A}^-}[\mathrm{A}^-]+L_{\mathrm{B}^+}[\mathrm{B}^+] \qquad (6)$$

where L_{H^+}, L_{OH^-}......are the mobilities of the ions. As L_{H^+} and L_{OH^-} are of the same order of magnitude and $[\mathrm{H}^+]\ll[\mathrm{OH}^-]$, $L_{\mathrm{H}^+}[\mathrm{H}^+]$ is negligible when compared to $L_{\mathrm{OH}^-}[\mathrm{OH}^-]$. Although of course $[\mathrm{A}^-]$ and $[\mathrm{B}^+]$ are not equal because of the hydrolysis, for simplicity we may be able to assume $[\mathrm{A}^-]\fallingdotseq[\mathrm{B}^+]$, as the value of L_{A^-} is, as expected, not very large. Then

$$\kappa\cdot10^3=L_{\mathrm{OH}^-}[\mathrm{OH}^-]+(L_{\mathrm{A}^-}+L_{\mathrm{B}^+})0.01\alpha_t$$

Here, $L_{\mathrm{OH}^-}=174$ and $L_{\mathrm{Na}^+}=43$. The value of L_{A^-} is of course not known but as the mobility of large organic anion is not expected to be so large as that of, for example, sodium ion, L_{A^-} is assumed for simplicity to be 10 in the above equation. Then,

$$\kappa\cdot10^3\fallingdotseq174[\mathrm{OH}^-]+0.53\alpha_t \qquad (7)$$

This equation 7 represents the conductometric titration curve. It is clearly shown that because of hydrolysis the measured conductivity lies higher by $174[\mathrm{OH}^-]$ over the salt line $0.53\alpha_t$. Relations between κ and α_t calculated for various pK phenols having different pK values are shown in Fig. 12.

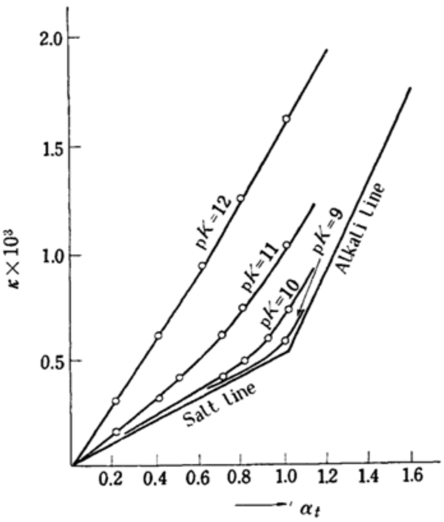

Fig. 12. Theoretically obtained conductometric titration curves of phenols having various p*K* values.

It is clearly demonstrated in this figure that one can calculate the equivalent point in so far as the p*K* values of the acids are smaller than 10, it being however quite impossible to find out the equivalent point when p*K* values are larger than 10. The difference of only about one unit in the p*K* values near p*K* 9∼11 definitely decide whether the phenol in question is conductometrically titratable or not. As the calculated titration curve for p*K* 12 is nearly linear, it is expected that the p*K* value of phenolic hydroxyl group of type II may be 12 or larger.

Experimental

Model Compounds IV, V and VI.—Compounds IV and VI were synthesized as reported previously[7]. Compound V was prepared according to Richtzenhain[8]. The sulfonic acid was separated as its benzylthiuronium salt was not crystallizable.

Anal. Found: C, 54.14; H, 5.58. Calcd. for $C_{26}H_{30}O_9N_2S_2$: C, 54.08; H, 5.58%.

Synthesis of α-(3, 4-Dimethoxyphenyl)-β-(2-hydroxy-3-methoxy-5-propylphenyl)-*n*-propanesulfonic Acid (VII).—Dihydro-dehydro-di-isoeugenol methyl ether (5 g.) was dissolved in 500 ml. of cooking acid (to 25 g. of sodium hydroxide in one liter of 50% alcohol was added 30 g. of sulfur dioxide after having been neutralized to pH 6 with sulfur dioxide) and heated in a vigorously rotating stainless autoclave for 20 hours at 135°C with a little amount of copper powder. After filtration, excessive sulfur dioxide was expelled in vacuo, sulfuric acid added, sulfur dioxide expelled and the solution was set aside over-night in order to decompose thiosulfate if any, after having adjusted the concentration of excess sulfuric acid to one normal. Sodium was removed by ion exchange, and the solution was concentrated, neutralized with barium carbonate, filtered, concentrated to dryness and extracted with water. A concentrated solution of benzylthiuronium hydrochloride was added to the extract thus obtained and the viscous precipitate of benzylthiuronium salt was washed with water, dissolved in a little amount of alcohol and reprecipitated with water. After having been purified twice by reprecipitation, the precipitate was rubbed with ice water. The powder thus obtained was not crystallizable.

Anal. Found: C, 58.98; H, 6.51; N, 5.11. Calcd. for $C_{29}H_{38}O_7N_2S_2$: C, 58.9; H, 6.49; N, 4.75%.

As the material was not obtained as crystals, the analytical values obtained did not agree well with the calculated values. Conductometrically the sulfonic acid group amounted to 92.5% of the theoretical amount. Without further purification the material was used for our purpose.

Synthesis of Dehydro-divanillyl Sulfonic Acid (VIII).—Although this compound is already known[9], no details are published as yet. Dehydro-divanillin was synthesized according to Elbs and Lerch[10]. It was found that dehydro-divanillin was very easily purified via its mono sodium salt. The crude product was dissolved in hot sodium hydroxide solution, which, upon cooling, separates beautiful crystals of mono sodium salt, which was recrystallized from aqueous alcohol.

Anal. Found: C, 59.21; H, 4.54; Na, 6.83. Calcd. for $C_{16}H_{13}O_6Na$: C, 59.3; H, 4.08; Na, 7.10%.

Dehydro-divanillin was dissolved in the least amount of dilute alkali, reduced with an exess of sodium borohydride until free from aldehyde color-reaction, acidified with carbon dioxide and the separated crystalline dehydro-divanillyl alcohol was filtered, m. p. 190°C.

Anal. Found: C, 62.51; H, 6.06; OCH_3, 20.32. Calcd. for $C_{16}H_{18}O_6$: C, 62.8; H, 5.89; OCH_3, 20.26%.

Dehydro-divanillyl alcohol thus obtained (2 g.) was shaken at 100°C for two hours in a sodium-base sulfite cooking acid of pH 1.8 (100 ml.). Dehydro-divanillyl sulfonic acid was separated as barium salt just as in the case of vanillyl sulfonic acid.

Anal. Found: C, 31.54; H, 3.58; S, 10.5; Ba, 22.42; OCH_3, 10.69. Calcd. for $C_{16}H_{16}O_{10}S_2Ba$: C, 33.7; H, 2.81; S, 11.2; Ba, 24.1; OCH_3, 10.69%.

Synthesis of Dehydro-divanillyl Alcohol Monomethyl Ether. Monosulfonic Acid (IX) and Disulfonic Acid (X) of the Monoether.—Dehydro-divanillin monomethyl ether[1]

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[7] H. Mikawa et al., This Bulletin, **29**, 245 (1956).

[8] Richtzenhain and Alfredsson, *Acta Chem. Scand.*, **8**, 1519 (1954).

[9] E. Adler and S. Hernestam, ibid., **9**, 319 (1955).

[10] K. Hlbs and H. Lerch, *J. prakt. Chem.*, **93**, 1 (1916).

was dissolved in a calculated amount of sodium hydroxide, reduced with excessive sodium boronhydride over-night until free from aldehyde color-reaction, neutralized with diluted hydrochloric acid and extracted exhaustively with chloroform. The oily product thus obtained in nearly theoretical yield was not crystallizable.

The oily dehydro-divanillyl alcohol monomethyl ether obtained was sulfonated at pH 1.9 for four hours at 100°C by sodium-base sulfite cooking acid. The crystalline barium salt separated as usual was not analyzed, however the strong acidic group amounting to 112% of the sulfonic acid group calculated from the formula IX was conductometrically titrated. This crystalline barium salt may, therefore, be contaminated a little by disulfonic acid X.

In order to prepare disulfonic acid X dehydrodivanillyl monomethyl ether was sulfonated at 135°C for five hours with the same cooking acid as above. As usual the disulfonic acid was isolated as barium salt. Conductometric titration of the acid revealed the existence of a strong acidic group amounting to 98.8% of the calculated amount.

Summary

1. Conductometric titrations of the model compounds IV, V, VI and VII provided reconfirmation of the previously reported[1] findings that simple guaiacol-type phenolic hydroxyl group I was conductometrically titratable, while non-guaiacyl phenolic hydroxyl group belonging to type II was conductometrically untitratable.

2. It was thus further confirmed, that the separate estimation of both type-I and -II phenolic hydroxyl groups of lignosulfonic acid by the method of conductometric titration is possible in combination with the ultraviolet absorption spectra taken simultaneously with the conductometric titration without any dilution of the solution.

3. As we have now considerable accumulation of facts supporting the existence of *o, o'*-diphenol type phenolic hydroxyl group in lignin, three water-soluble model compounds VIII, IX and X were titrated conductometrically. Phenolic hydroxyl groups of IX and X were found to be conductometrically titratable. Of the two phenolic hydroxyl groups of the model compound VIII only one was found to be titratable.

4. A brief theoretical consideration of the conductometric titration of extremely weak acid (phenol) having pK values larger than 9 were made. As is evident from Fig. 12, which shows theoretical conductometric titration curves of phenols having pK values 9~12, one can calculate the equivalence-point in so far as the pK values of the phenols are smaller than 10; it is, however, impossible to find the equivalence-point when pK values are larger than 10. As the calculated titration curve for pK 12 is nearly linear, it is expected that the pK value of phenolic hydroxyl group of type II is 12 or larger.

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