On the Phenolic Hydroxyl Group of Lignosulfonic Acid and the Existence of Carboxyl Group in Lignosulfonic Acid

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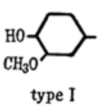
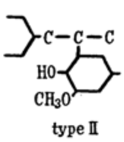
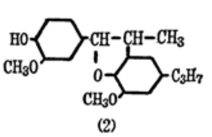
The amount of the phenolic hydroxyl group of lignin in situ was estimated from the difference of the phenolic hydroxyl group content of the lignothioglycolic acid prepared from untreated wood and methylated wood. The amount was found to be about one OH* per 5.3 CH_3O. Wood powder sulfonated at neutral pH contains lignosulfonic acid, called solid lignosulfonic acid, which has sulfonic acid group only at X and Z groups of lignin[1]. The phenolic hydroxyl group content of the soild lignosulfonic acid was also measured in the same way with the wood power sulfonated at neutral pH, and was found to be the same as that of the lignin in situ. It was, therefore, found that the sulfonation of lignin at neutral pH causes no increase of the phenolic hydroxyl group of lignin. The "low sulfonated lignosulfonic acid" prepared from the sulfonated wood by Kullgren process was also found to have nearly the same amount of the phenolic hydroxyl group as the lignin in situ. The phenolic hydroxyl group of the low sulfonated lignosulfonic acid is, therefore, the one already present in the lignin in situ. The amount of the phenolic hydroxyl group of these lignin preparations was estimated spectroscopically according to the method of Aulin-Erdtman[2].

The nature of the conductometrically observed weakly acidic group of α-lignosulfonic acid was not definitely known, being thought to be phenolic or carboxylic in nature[3]. It was reported recently[4] that this group consisted of nearly equal amounts of carboxyl and phenolic hydroxyl groups. It was also reported, that only about 30 % of the total phenolic hydroxyl group of α-lignosulfonic acid, was ionized before the second "break", i. e. conductometrically titratable, the remaining 70 % being too weak to be titrated. From the following experimental findings it was concluded that the former conductometrically titratable group is of simple guaiacol (type I) and the latter untitrable one is of type II.


type I


type II


(2)

Conductometric titrations of many model compounds showed that the phenolic hydroxyl group of type I was without exception titratable. For example, phenolic hydroxyl group of vanillyl sulphonic acid and one of the phenolic hydroxyl groups of compound (1), which belongs to type I were titratable (cf. Fig.), while the other belonging to type II was not. As the existence of these two types of phenolic hydroxyl groups in lignosulfonic acid is quite probable, it may reasonably be concluded that the conductometrically un-

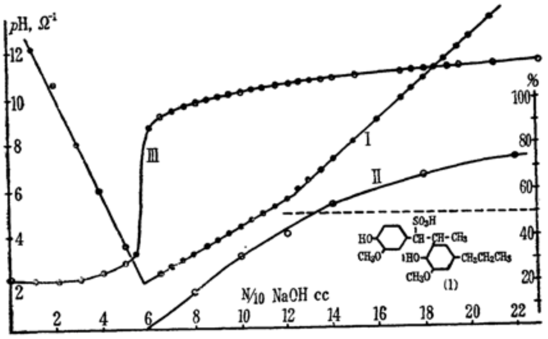


Fig. 1. Trtrations of model compound (I). I conductometric titration, III potentiometric titration, II percentage of the ionized phenolic hydroxyl groups of the compound.

titratable phenolic hydroxyl group of lignosulfonic acid belongs to type II.

Coductometric titration of the so-called low sulfonated lignosulfonic acid revealed that the ratio of the phenolic hydroxyl groups of type I and II was about 1: 1. As stated previously the phenolic hydroxyl group of this acid is the same as that of the lignin originally present in wood. For this reason the phenolic hydroxyl group of lignin in wood may contain these two types in approximately equal amounts. The content of type I is higher in heach α-lignosulphonic acid than in spruce α-acid, the ratio of type I and II being about 1: 1.

Synthesis of sulfonic acid (1)

Dihydro-dehydrodiisoeugenol (2) (4.7 g.) was dissolved in 50 ml. of 50 % aqueous alcohol containing NaOH (0.85 g.) and SO_2 (2.5 g.), kept at 140° for twenty hours. The sulfonic acid (1) was separated as benzylthiuroniumsalt. Repeated recrystallization raised the m.p. to 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 $C_{28}H_{36}O_7N_2S_2$ (benzylthiuronium salt of (1)): C, 58.3; H, 6.24; N, 4.86; CH_3O, 10.75 %

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