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MONOMERIC LIGNIN SULPHONIC ACIDS

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In a review of lignin chemistry in 1956 Smith[1] stated that the prospect of isolating some of the simpler lignin sulphonic acids by chromatographic procedures seemed to be quite good. Since then, the isolation of 1-(3-methoxy-4-hydroxyphenyl)-2-propene-1-sulphonic acid and 1-(3-methoxy-4-hydroxyphenyl)-1-propene-3-sulphonic acid from commercial spent sulphite liquor has been achieved at the University of Washington, and these structures have been confirmed by the N.M.R. studies of Ludwig[2].

In this laboratory six lignin sulphonic acids have been isolated from spent sulphite liquor obtained from the pulping of wattle wood (*Acacia mearnsii*, formerly *A. mollissima*). The same acids have been shown, by paper chromatography, to be present in a sample of "Orzan A" (Crown Zellerbach Corp.) and it is probable that they occur in spent sulphite liquor from any hardwood. These acids were separated from those of higher molecular weight by absorption on the sulphate form of an anion-exchange resin[3]. They were then eluted with dilute sulphuric acid, and the sulphate ion was removed by precipitation with barium carbonate. This solution was a complex mixture, but paper chromatography in n-butanol-acetic acid-water-pyridine (Waley's solvent[4]), followed by a spray of diazotized p-nitraniline in 8% hydrochloric acid, revealed six spots. These substances were separated from each other by preparative paper chromatography, but were found still to be impure. Larger amounts of these acids were separated by ion-exchange chromatography, and these were purified by repeated chromatography of their sodium salts on silica gel and on "Florisil" with wet n-butanol, or the isopropanol-water azeotrope, as eluants. The acids were numbered in order of decreasing R_F value of their sodium salts in Waley's solvent at 20° on Whatman No. 1 paper.

TABLE

Substance No.	I	II	III	IV	V	VI
R_F (Waley's solvent)	.67	.62	.47	.44	.30	.26
R_F (butanol:pyridine:water, 6:4:3)	.27	.26	.17	.16	.03	.02
M.p. of aniline salt	209°	198.5°	129°			

Compounds I, II, and III have been obtained crystalline and analytically pure. The other three have not, but they have been characterized by their R_F values in six different solvent systems.

STRUCTURE

Molecular weight measurements (with "Mechrolab" vapour pressure osmometer) showed that with the exception of V, all compounds had molecular weights of about 300. Equivalent weights of I, II, and III were found to be 302, 302, 329. (Required 296, 298, 330). Oxidation[5] produced syringaldehyde as the only aromatic aldehyde. The structures of I and II then followed from their N.M.R. spectra. Chemical evidence for the double bond in II was obtained by hydrogenation, when II took up one mole of hydrogen to give I.

$Ar.CHSO_3Na.CH_2.CH_3$	I
$Ar.CHSO_3Na.CH{:}CH_2$	II
$Ar.CHSO_3Na.CHOH.CH_2OH$	III, IV
$Ar.CH_2.CHSO_3Na.CH_2OH$	VI

where Ar = syringyl

All the compounds gave a negative test with quinone monochlorimide, and therefore any hydroxyl groups present were not attached to the benzylic carbon atom[6]. Compound III was therefore one of the diastereoisomers of sodium 1-(4-hydroxy-3,5-dimethoxyphenyl)-propan-2,3-diol-1-sulphonate. When synthetic "syringylglycerol" was heated with sodium bisulphite solution, III and IV were produced in similar amounts. Both compounds were formed from either diastereoisomer of "syringylglycerol", and the synthetic compounds were shown to be identical with those isolated from spent sulphite liquor, by paper chromatography in five different solvent systems. It is not known which isomer has the *threo*- and which the *erythro*- configuration.

When III or IV was heated with a solution of sulphur dioxide and sodium bisulphite (pH 1.6) at 140°, some starting material was unchanged, but some was converted to a sulphonic acid (VII) which had an R_F value 1.14 times that of VI in Waley's solvent. I was found, too, in the reaction product from III, but not in that from IV. The mechanism of this unusual reduction is unknown. Compound VII has not been isolated from spent sulphite liquor, but it must be present in the liquor since it is formed from III or IV under cooking conditions. When sinapyl alcohol was allowed to react with sodium bisulphite solution in the presence of free radicals, and at room temperature, the main product was VI. Sodium 1-(4-hydroxy-3,5-dimethoxyphenyl)-propan-3-ol-2-sulphonate would be expected to result from this reaction, and VI most probably has this structure. Paper chromatography showed the presence of three impurities in the reaction product, and one of these had an R_F value very similar to that of VII. This indicates that VII may be sodium 1-(4-hydroxy-3,5-dimethoxyphenyl)-propan-3-ol-1-sulphonate, which could be formed by the reverse addition of sodium bisulphite to sinapyl alcohol, and also by the reduction of the secondary hydroxyl group in III or IV.

Compound V is believed to be a dimer of VI. Full details of this work, and of synthetic experiments now being undertaken, will be published later.

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