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The Reactions of Lignin during Neutral Sulfite Pulping. Part VIII.* Sulfonic Acids Isolated after Treatment of Spruce Wood Meal with Neutral Sulfite

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The behaviour of the main structural elements of lignin under the conditions of neutral sulfite pulping has been the subject of extensive model experiments.[2-6]

The present work is concerned with the isolation and identification of some of the main monomeric sulfonic acids formed during the treatment of finely divided wood with neutral sulfite.

Spruce wood meal (200 g), pre-extracted with acetone, was treated with a solution of sodium sulfite (120 g) in water (1600 ml) at 180 °C for 3 h in a stainless steel autoclave (initial pH ~ 10, final pH ~ 7). The resulting pulp (120 g; lignin content according to Klason 15.7 %) was washed with water and the total liquor concentrated to 2000 ml. Continuous extraction with methylene chloride removed 840 mg of lipophilic material. This was not investigated further. To the remaining aqueous solution, Hyamine 10-X ** (80 g) was added to precipitate polymeric lignosulfonic acids.[7] After centrifugation, tetrabutylammonium sulfate (80 g) was added to the remaining solution. The low-molecular weight lignosulfonic acids were continuously extracted as ion pairs [8] with methylene chloride. Evaporation of the solvent gave a mixture of sulfonates which were acetylated with acetic anhydride-pyridine (1:1) at room temperature. Excess acetic anhydride and pyridine were removed by evaporation under reduced pressure and water was added. The aqueous suspension was treated with active carbon to remove undissolved material (probably acetylated carbohydrates) and the acetylated sulfonic acids were then converted into methyl esters (23.6 g) as previously [9] described. Column chromatography on silicic acid (Bio-Sil A 100 – 200 mesh, Bio-Rad Lab., Richmond, California) using ethyl acetate as solvent removed 3.6 g of polymeric material. The remaining low-molecular weight acetylated sulfonic acid methyl esters were separated in a liquid chromatograph (Chromatromix Inc., Berkeley, California) using silicic acid (Bio-Sil A 200 – 325 mesh) as the stationary phase. The flow rate in a 25.4 × 1000 mm column was 1 ml/min. The individual sulfonic acid esters were identified by comparing the ^{1}H NMR and mass spectra with those of authentic samples (for references, see below).

The mixture of sulfonates was first separated using cyclohexane-ethyl acetate (1:1) as solvent system. Four fractions were obtained in yields of 1.6, 6.2, 2.7 and 4.9 g. On further column chromatography, only fractions 2 and 4 gave pure components. The composition of the other fractions was too complex to allow successful separation.

Fraction 2 (6.2 g) was subjected to chromatography but now using cyclohexane-ethyl acetate (3:2) as solvent system. Five subfractions were obtained in yields of 360, 160, 1060, 945 and 1285 mg.

Subfraction 3 (1.06 g) was further chromatographed using cyclohexane-ethyl acetate (7:3) as solvent system. Pure methyl methanesulfonate [6] (300 mg) was obtained. ^{1}H NMR: δ 2.96 (s, 3 H, Me), 3.84 (s, 3 H, OMe).

* Part VII, see Ref. 1.

** Benzyldimethyl {2-[2-(*p*-1,1,3,3-tetramethylbutylcresoxy)ethoxy]ethyl}ammonium chloride monohydrate (Rohm and Haas Co.).

Subfraction 4 (945 mg) was also separated using the same solvent system. Two fractions were obtained in yields of 200 and 410 mg. In the first fraction, α-methoxysulfonyl-β-acetoxymethyl-4-acetoxy-3-methoxystyrene (*1*) [2] was present as major component. The second fraction contained mainly dimethyl 1-(4-acetoxy-3-methoxyphenyl)-ethane-1,2-disulfonate (*2*).[2,4] In both fractions the main component was accompanied by small amounts of methyl 1,2-di-(4-acetoxy-3-methoxyphenyl)-ethane-1-sulfonate (*3*),[3] as indicated by the mass spectra.

Subfraction 5 (1285 mg) was separated using cyclohexane-ethyl acetate (3:2) as solvent system. Two fractions (315 and 110 mg) were obtained, both containing compound *2* as major component. Mass spectral fragmentation of the first and second fraction indicated the presence of small amounts of compound *3* and methyl 1-(4-acetoxy-3-methoxyphenyl)-3-acetoxypropane-1-sulfonate (*4*),[1] respectively.

Fraction 4 (4.9 g) was separated using cyclohexane-ethyl acetate (2:3) as solvent system. One component could be obtained in pure form and identified as dimethyl 1-(4-acetoxy-3-methoxyphenyl)-propane-1,3-disulfonate (*5*) [10] (2200 mg).

The sulfonic acids hitherto isolated and identified as their acetylated methyl esters (*1* – *5*) are the dominating monomeric components of the resulting complex reaction mixture (TLC). They are all products expected to be formed by neutral sulfonation of known structural elements [11] of the "uncondensed" [12] type. Thus, compounds *1* and *2* should arise from terminal (=phenolic) or inner (=non-phenolic) arylglycerol-β-aryl ether structures.[2] Compound *3* should originate from 1,2-diaryl-propane-1,3-diol structures,[3] and compounds *4* and *5* from end groups of the coniferaldehyde [1] and coniferyl alcohol [10] types, respectively. The formation of compounds *1* – *5* presupposes the existence or the sulfitolytic liberation of the respective structure as a free phenol.

The isolation of these compounds supports the validity of the sulfonation schemes proposed for the aforementioned structural elements on the basis of the results from model studies.[1–4] Additional acids suggested in these schemes are likely to be present, albeit in minor amounts, in the fractions not successfully separated so far.

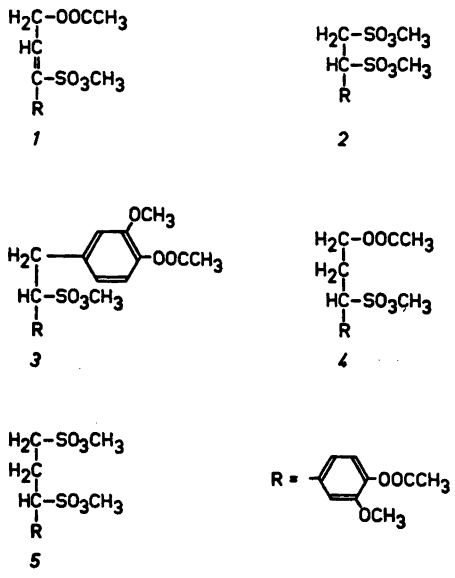

Fig. 1. Acetylated sulfonic acid methyl esters isolated after treatment of spruce wood meal with neutral sulfite, acetylation, methylation and column chromatography.

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