The Reactions of Lignin during Neutral Sulfite Pulping.
Part VII.* The Behavior of Structural Elements Containing Carbonyl Groups

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The reactions of carbonyl-containing lignin units of the coniferaldehyde (A), phenacyl aryl ether (B) and glyceraldehyde-α-aryl ether (C) types with neutral sulfite under technical conditions have been investigated.

All three types undergo extensive sulfonation and suffer cleavage of aryl alkyl ether bonds. These reactions result in the removal of the aldehydic groups in end units (types A and C), in the separation of adjacent units (type B) and in the formation of potential chromophoric groups of the catechol type (types A, B and C).

The significance of these reactions for the behaviour of lignin in neutral sulfite pulping is briefly discussed.

It is known that carbonyl-containing units in lignins participate in the sulfonation process in acidic media. In particular, structural elements containing conjugated carboxyls, such as coniferaldehyde (A), and the 1,3-keto (B) type of structure, have been shown to undergo sulfonation. Aldehydic groups in "detached" side chains (C), which constitute another type of 1,3-ketol structure, have been suggested to react in a way analogous to type B.

In continuation of our work on the reactions of lignin during neutral sulfite pulping, the behaviour of carbonyl-containing model compounds representing the structural types A – C under the conditions of this pulping process has now been studied.

RESULTS AND DISCUSSION

(a) Neutral sulfonation of coniferaldehyde and of coniferaldehyde methyl ether. After treatment of coniferaldehyde (I) with neutral sulfite, two monosulfonic acids (5 and 8) and one disulfonic acid (12) were isolated as the acetylated methyl esters (see Experimental). Plausible pathways of formation for these main products are outlined in Scheme 1.

It is suggested that compounds 5 and 8 are formed by a hydride transfer, the doubly charged bisulfite addition product 2 acting as hydride donor and the aldehydic α-sulfonic acid 3 as acceptor. The dehydrogenated product (4), being an α-keto sulfonic acid, readily undergoes hydrolytic cleavage affording ferulic acid (6). The latter, probably in the tautomeric quinone methide form which is a vinyllogous β-keto acid, loses carbon dioxide and the resulting 4-vinylguaiaicol (7) adds bisulfite to give sulfonic acid 8. The facile conversion of ferulic acid (6) into 8 was shown in a separate experiment using similar sulfonation conditions. The hydrogenated product (5) was isolated. Disproportionation of compound 1 prior to sulfonation can be excluded since the reduced

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* Part VI, see Ref. 1.

product, coniferyl alcohol, under the conditions used, would yield the corresponding α,γ-disulfonic acid (cf. also Ref. 10).

The formation of the disulfonic acid 12 is suggested to be initiated by the sulfitolytic demethylation (SDM) of 1 to give 9, followed by ring closure to yield 1,5,6-trihydroxyindene (10). The latter may be regarded as a cyclic dihydroxydehydrocinnamyl alcohol which is able to form the extended cyclic quinone methide 11. A 1,8- (or 1,6-) and a subsequent 1,2- (or 1,6-) addition of bisulfite gives the symmetrical dihydroxydisulfonic acid 12. The behaviour of the hypothetical trihydroxyindene (10) towards neutral sulfite is thus analogous to that of (acyclic) p-hydroxybenzaldehyde, like coniferyl alcohol, and of β-aryl-substituted p-hydroxybenzyl alcohol (α-hydroxymethyl-substituted stilbenes).1

Similar demethylation and subsequent cyclization reactions of the coniferaldehyde type of units should also take place upon treatment with other strong nucleophiles (e.g., hydrogen sulfide ions). However, the reactions can only be demonstrated if the trihydroxyindene intermediate is immediately trapped to give a stable compound (e.g., by sulfonation) and thus prevented from polymerization.

Treatment of 1 with acidic sulfite afforded the aldehydic sulfonic acid 3 which decomposed during the attempted separation and purification (as the acetylated methyl ester). The formation of coniferaldehyde hydroxysulfonic acid groups (3) during sulfonation has been previously supported by numerous model experiments and compound 3 has been detected as the sodium salt in the spent liquor from the treatment of red alder with acidic sulfite.11

Coniferaldehyde methyl ether (13), similarly treated with neutral sulfite, afforded the sulfonic acids, 5, 8, 14, 16 and 17 as major products (Scheme 2). The phenolic α-sulfonic acids 5 and 8 are apparently formed from 1 by the route shown in Scheme 1. Compound 1 arises from the

Scheme 1. Neutral sulfonation of coniferaldehyde (I). In this and the following schemes the sulfonic acids are depicted as anions. Isolated products are framed. SDM = sulfitolytic demethylation.
starting compound (13) by partial sulfitolytic demethylation. Further sulfitolytic demethylation of 1 should ultimately result in the formation of the dihydroxyindanedisulfonic acid 12 as outlined in Scheme 1. However, this expected sulfonation product was obviously formed from 13 in such a small amount that it was not found in the reaction mixture. The formation of compounds 16 and 17 may again be explained by a hydrogen transfer. The (isolated) disulfonic acid (14), formed by addition of 2 mol of bisulfite to 13, serves as hydride donor and the aldehydic α-sulfonic acid 15, formed by addition of 1 mol of bisulfite to 13, as acceptor.

The mechanism of formation of 16 and 17 is thus analogous to that proposed for the formation of ferulic acid (8) and of compound 5, respectively (Scheme 1). However, unlike ferulic acid, the non-phenolic carboxylic acid 16, formed by hydrolysis of the corresponding α-keto sulfonic acid intermediate, cannot undergo decarboxylation.

Compound 13 is a vinlylog of veratraldehyde which has been reported to be in part oxidized by bisulfite to give veratric acid. Attempts to find veratryl alcohol, which would be the reduced product in the case of a disproportionation, have been unsuccessful.

In addition to the sulfonic acids depicted in Scheme 2, the reaction mixture from compound 13 also contained small amounts of 1-(4-hydroxy-3-methoxyphenyl)-3-hydroxypropene-1,3-disulfonic acid, obviously formed by sulfitolytic demethylation of 14, and of its dehydration product, 1-(4-hydroxy-3-methoxyphenyl)-2-propene-1,3-disulfonic acid.

(b) Neutral sulfonation of the 1,3-ketol 18. Treatment of compound 18 (Scheme 3) with neutral sulfite resulted in extensive sulfitolytic cleavage of the alkyl aryl ether bonds. This was revealed by the high yield of methanesulfonic acid and by the phenol nature of the majority of the other reaction products. Besides methane-

Scheme 2. Neutral sulfonation of coniferaldehyde methyl ether (13).

Scheme 3. Neutral sulfonation of 1-(3,4-dimethoxyphenyl)-2-guaiacoxo-3-hydroxypropene-1-one (18).

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sulfonic acid, the keto sulfonic acids 22 and 25 were the main components of the water-soluble fraction (see Experimental). The formation of these keto sulfonic acids is tentatively outlined in Scheme 3. Demethylation is suggested to be the initial step of the formation of 22. The resulting phenolic 1,3-ketol intermediate 19 loses one molecule of water to give the unsaturated ketone 20. The latter adds bisulfite affording the keto sulfonic acid 21 which, by a β-elimination, loses the aroxy substituent as guaiacol to yield 22. The other keto sulfonic acid (25) obviously arises by elimination of formaldehyde from either the starting compound 18 or its demethylation product 19, followed by sulfitolytic cleavage of the phenacyl aryl ether linkage in 21. The latter reaction step was demonstrated by treating authentic 24 with neutral sulfite and isolating 25 in high yield.

It has previously been reported that compound 18, when treated with a sulfite solution of pH 6 at 155 °C for 5 h, gives a fair yield of the corresponding keto sulfonic acid (21, with R² instead of R¹). This non-phenolic sulfonic acid was not obtained in the neutral sulfonation of the present work, obviously due to the different conditions used (pH 7, 180 °C, 3 h). Under these conditions, sulfitolytic demethylation of 18 and elimination of guaiacol from the suggested intermediate 21 appear to dominate. Treatment of 18 with acidic sulfite (cf. also Ref. 5) afforded the keto sulfonic acid (21, with R¹ instead of R) in a yield of about 25 %.

The chloroform-ether soluble fraction from the neutral sulfite treatment of 18 contained small amounts of guaiacol, bis(4-hydroxy-3-methoxyphenyl)methane (26) and aceto- veratrone (32) as well as the demethylation products catechol, α-guaiacoxacyetoguaiacone (24), compounds 27–29, acetoguaiacone (30) and its isomer (31).

The formation of compound 24 has already been discussed. Compounds 26 and 27 arise by condensation of the eliminated formaldehyde with guaiacol (27) or with guaiacol and catechol (26). The formation of acetoeveratrone (32) must involve the reductive cleavage of the phenacyl aryl ether bond in 23. Acetoguaiacone (30) and its isomer (31) are formed by partial sulfitolytic demethylation of 32.

Phenolic structures of type B should behave like compound 19, an intermediate in the formation of the unsaturated keto sulfonic acid 22.

Neutral sulfonation of (2-methoxyphenoxy)-acetaldehyde (33). Like the carbonyl compounds 1, 13 and 18, compound 33 undergoes extensive cleavage of the alkyl aryl ether linkages when treated with neutral sulfite. Considerable amounts of guaiacol and catechol were found in the chloroform-ether extract. The water-soluble fraction contained several low-molecular constituents as well as polymeric material. Methanesulfonic acid and 1-(2-methoxyphenoxy)ethane-1,2-disulfonic acid (37, Scheme 4) were isolated from this fraction. The formation of the latter product is suggested to proceed via bisulfite-addition to the aldehydic group, elimination of water from the resulting α-hydroxy sulfonic acid (35) and a further bisulfite addition across the double bond in 35. Attempts to isolate the unsaturated sulfonic acid 38, expected to be formed by elimination of guaiacol from 37, were unsuccessful.

Compound 34, a better model for the detached side-chain structures of type C, behaves similarly when treated with neutral sulfite. Large amounts of cresol and 4-methyl catechol were obtained, indicating an almost quantitative cleavage of the 2-aryl ether bond and a partial cleavage of the methyl aryl ether bond in 34. The water-soluble fraction contained methanesulfonic acid and a high-molecular weight material, probably formed by polymerization of unsaturated sulfonic acids arising by a course of reaction analogous to that shown in Scheme 4.

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generation of potential chromophores of the catechol type. An analogous behaviour has recently been observed with intermediates of the stilbene type.

The fragmentation due to the cleavage of phenacyl aryl ether bonds in structural elements of type B may be partly compensated by the condensation of the liberated formaldehyde with phenolic structures. The expected formation of benzyl sulfonic acids, arising by condensation of hydroxymethanesulfonic acid with phenolic structures or by sulfonation of benzyl alcoholic structures (cf. Ref. 15), was not observed in these experiments, presumably due to the somewhat lower pH used.

EXPERIMENTAL

Melting points are corrected. Evaporations were carried out under reduced pressure.

Model compounds. The model compounds used were prepared as previously described: $J^{14}$, $6^1$, $17^1$, $18^1$, $15^3$, $33^1$, $34^1$, $36^1$.

**Sulfite treatment, work-up procedure, chromatographic, $^1H$ NMR and MS methods** have been previously described.$^{36,15}$

$^1H$ NMR spectra. The spectra of the chloroform-ether soluble products and the acetylated sulfonic acid methyl esters showed all the expected signals exhibited by aromatic and olefinic protons (range: $\delta$ 6.6–7.9), methoxyl protons (ester and ether) (range: $\delta$ 3.5–3.9), aliphatic protons (range: $\delta$ 2.6–5.9) and acetoxyl protons (aromatically bound: $\delta$ 2.25–2.32, aliphatically bound: $\delta$ 2.0–2.1).

The chemical shifts and the integrals of the signals were all in agreement with the proposed structures.

**Mass spectra.** The methyl esters of the (acetylated) sulfonic acids gave peaks of varying intensity for the molecular ions. The main fragmentations are due, in the order given, to the losses of keton ($-42$) from aromatic acetyl groups, of $SO_3CH_2$ ($-98$) or $HSO_4CH_2$ ($-96$) from aliphatic sulfonic acid methyl ester groups and of acetic acid ($-60$) from aliphatic acetyl groups.

Treatment of model compounds with sulfite solutions

The following (acetylated) sulfonic acid methyl esters were isolated (Table 1) and

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* Part of the compound 34 used in this work was prepared by Dr. Tapio Hase, Leila Lahtinen and Aarne Klemola, Helsinki, Finland, following an improved synthetic procedure (see Acta Chem. Scand. B 31 (1977) 501), and kindly put at our disposal.
Table I. Treatment of model compounds containing carbonyl groups with sulfite solutions.\(^a\)

<table>
<thead>
<tr>
<th>Compound (mg)</th>
<th>Conditions</th>
<th>Products (mg)</th>
<th>Sulfonic acids, isolated as (acetylated) methyl esters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Chloroform-ether extract</td>
<td></td>
</tr>
<tr>
<td>1 (500)</td>
<td>NS</td>
<td>(60); SM, P</td>
<td>(225); (\delta) (155), (\delta) (290) (m.p. 74.5–75.0(^\circ)) 12 (80), MSA+some P</td>
</tr>
<tr>
<td>1 (1000)</td>
<td>AS</td>
<td>(60); P</td>
<td>(920)  (^b)</td>
</tr>
<tr>
<td>13 (500)</td>
<td>NS</td>
<td>(60); V, VE</td>
<td>(1100); 5+ product of demethylation and dehydration from 14 (270),(^b) 8 (60), 14+product of demethylation from 14 (290),(^b) 16 (45) (m.p. 94.5–96.5(^\circ)), 17 (60), MSA</td>
</tr>
<tr>
<td>18 (1000)</td>
<td>NS</td>
<td>(450); G (250), C (25), 24 (35), 26+30 (65),(^b) 27+29 (40),(^b) 31+32 (26)(^b)</td>
<td>(1500); 22 (220) (m.p. 107.5–108.0(^\circ)), 25 (350), MSA</td>
</tr>
<tr>
<td>18 (500)</td>
<td>AS</td>
<td>(375); SM</td>
<td>Methylated 21 (150)</td>
</tr>
<tr>
<td>33 (2000)</td>
<td>NS</td>
<td>(1040); G, C</td>
<td>(1720); 37 (260), MSA (290), P</td>
</tr>
<tr>
<td>34 (1000)</td>
<td>NS</td>
<td>(665); Cr, MC</td>
<td>MSA, P</td>
</tr>
</tbody>
</table>

\(^{a}\) Abbreviations. Conditions: NS, treatment with neutral sulfite (pH 7) at 180 \(^\circ\)C for 3 h. AS, treatment with acidic sulfite (pH 1.5) at 155 \(^\circ\)C for 7 h. Products: C, catechol; Cr, cresol; G, guaiacol; MC, 4-methylcatechol; MSA, methansulfonic acid; P, polymeric material; SM, starting material; V, vanillin; VE, veratraldehyde.  \(^{b}\) The components were indentified by MS without complete separation from each other.

\(^\dagger\) Identified by the \(^1\)H NMR (60 MHz, CDCl\(_3\)) and mass spectral data given.

(1) After neutral sulfonation (pH 7, 180 \(^\circ\)C, 3 h) From compound 1:*  

1-(4-Acetoxy-3-methoxyphenyl)-3-acetoxypropane-1-sulfonic acid methyl ester (methyl ester of 5-diaceate). \(^1\)H NMR: \(\delta\) 1.98 (s, 3 H, Ac), 2.29 (s, 3 H, Ac), 2.6 (broad s, 2 H, CH\(_2\)), 3.67 (s, 3 H, OMe), 3.84 (s, 3 H, OMe), 4.2 (broad s, 3 H, CH\(_2\)OMe), 7.00 (3 H, ar). MS m/e (rel. int.): 380 (M, 6), 318 (M–42, 23), 223 (M–42–95, 10), 222 (M–42–96, 3), 163 (M–42–95–60, 100).  

1-(4-Acetoxy-3-methoxyphenyl)ethane-1-sulfonic acid methyl ester (methyl ester of 8-diaceate). m.p. 74.5–75.0\(^\circ\)C. \(^1\)H NMR: \(\delta\) 1.78 (d, 3 H, al. Me), 2.27 (s, 3 H, Ac), 3.67 (s, 3 H, OMe), 3.80 (s, 3 H, OMe), 4.33 (q, 1 H, CH), 7.00 (3 H, ar). MS m/e (rel. int.): 288 (M, 5), 246 (M–42, 25), 161 (M–42–95, 100), 150 (M–42–96, 27).  

5,6-Diacetoyindane-1,3-disulfonic acid dimethyl ester (dimethyl ester of 12-diaceate). \(^1\)H NMR: \(\delta\) 2.27 (s, 6 H, Ac), 3.09 (2 H, CH\(_2\)), 3.82 (s, 6 H 2x OMe), 4.92 (2 H, 2x CH).  


From compound 13:  

1-(4-Acetoxy-3-methoxyphenyl)-3-acetoxypropane-1-sulfonic acid methyl ester. For identification, see above.  

1-(4-Acetoxy-3-methoxyphenyl)ethane-1-sulfonic acid methyl ester. For identification, see above.  

1-(3,4-Dimethoxyphenyl)-3-acetoxypropane-1,3-disulfonic acid dimethyl ester (dimethyl ester of 14-diaceate). \(^1\)H NMR: \(\delta\) 2.13 (s, 3 H, Ac), 2.96 (broad s, 2 H, CH\(_2\)), 3.67 (s, 3 H, OMe), 3.87 (9 H, 3x OMe), 4.2 (broad s, 1 H, CH), 5.6 (broad s, 1 H, CH), 6.89 (3 H, ar). MS m/e (rel. int.): 426 (M, 9), 381 (M–95, 13), 271 (M–95–60, 26), 175 (M–95–60–96, 100).  

1-(4-Acetoxy-3-methoxyphenyl)-3-acetoxypropane-1,3-disulfonic acid dimethyl ester (dimethyl ester of demethylated 14-diaceate). MS m/e (rel. int.): 454 (M, 1), 412 (M–42, 9), 352 (M–42–60, 9), 317 (M–42–95, 9), 257 (M–42–95–60, 43), 161 (M–42–95–60–96, 100).  

1-(4-Acetoxy-3-methoxyphenyl)-2-propane-1,3-disulfonic acid dimethyl ester (dimethyl ester of demethylated and dehydrated 14-diaceate).

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* All compounds investigated here gave methanesulfonic acid methyl ester in addition to the sulfonic acid esters mentioned.
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compounds were isolated by TLC or LC (phenolic compounds as acetates) and identified by 1H NMR and/or GC-MS (comparison with authentic samples, if available): guaiacol, cresol, catechol, 4-methylcatehol, vanillin and veratraldehyde as well as compounds 24 and 26–32.

REFERENCES

8. See Ref. 2, p. 626.

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