# 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.[2] In particular, structural elements containing conjugated carbonyls, such as coniferaldehyde (A)[3,4] and the 1,3-keto] (B)[5] type of structure, have been shown to undergo sulfonation. Aldehydic groups in "detached" side chains (C),[6,7] which constitute another type of 1,3-ketol structure, have been suggested[8] to react in a way analogous to type B.

CHO
|
HC
‖
CH

H₂COH   OCH₃
|
HC–O–

H₂COH   OCH₃
|
HC–O–
|
HCO

OCH₃
|
OR

A

OCH₃
|
OR

B

C
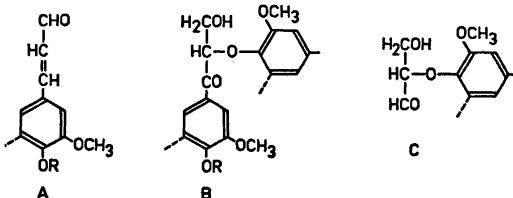
R = H or side chain
of the adjacent unit

* Part VI, see Ref. 1.

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 (1) 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 vinylogous β-keto acid, looses carbon dioxide and the resulting 4-vinylguaiacol (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
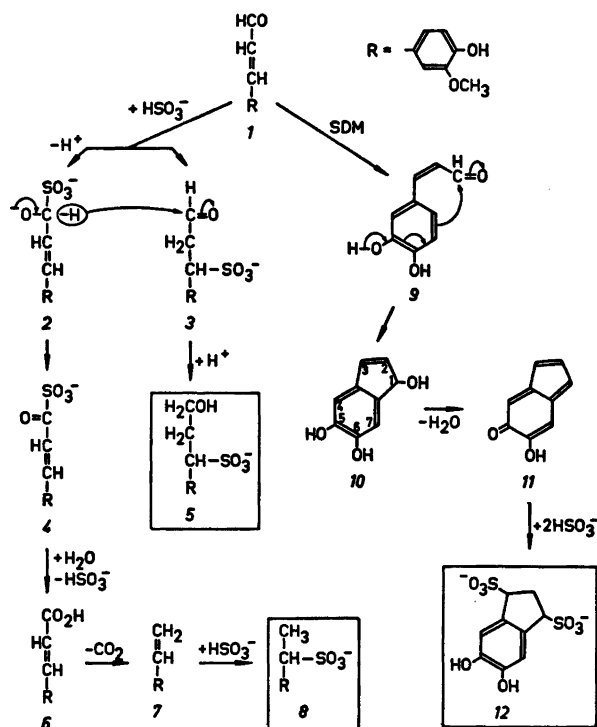
**Scheme 1.** Neutral sulfonation of coniferaldehyde (*1*). In this and the following schemes the sulfonic acids are depicted as anions. Isolated products are framed. SDM = sulfitolytic demethylation.

product, coniferyl alcohol, under the conditions used, would yield the corresponding $\alpha,\gamma$-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*-hydroxycinnamyl alcohols, like coniferyl alcohol,[9] and of $\beta$-aryl-substituted *p*-hydroxycinnamyl alcohols ($\alpha$-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 hydrosulfonic acid groups (*3*) during acidic 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 $\alpha$-sulfonic acids *5* and *8* are apparently formed from *1* by the route shown in Scheme 1. Compound *1* arises from the

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 com-
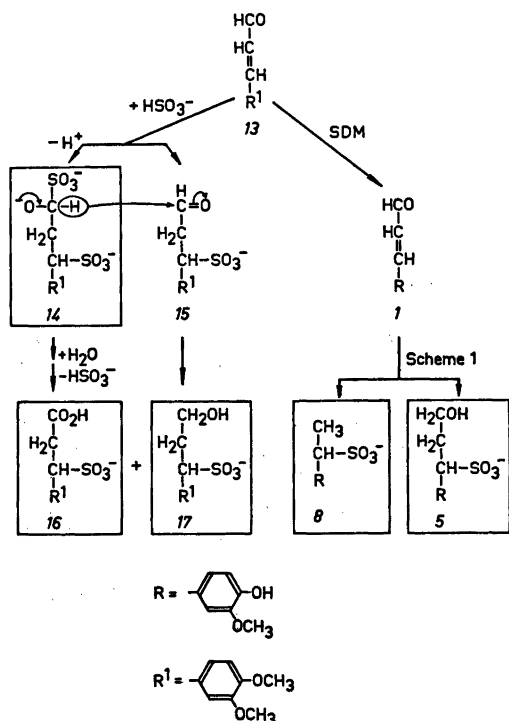


*Scheme 2.* Neutral sulfonation of coniferaldehyde methyl ether (*13*).

pounds *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 (*6*) 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 vinylog of veratraldehyde which has been reported [12] 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-hydroxypropane-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 phenolic nature of the majority of the other reaction products. Besides methane-
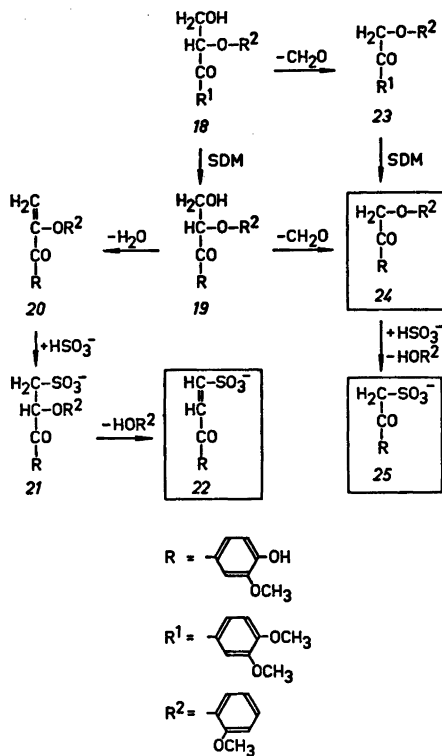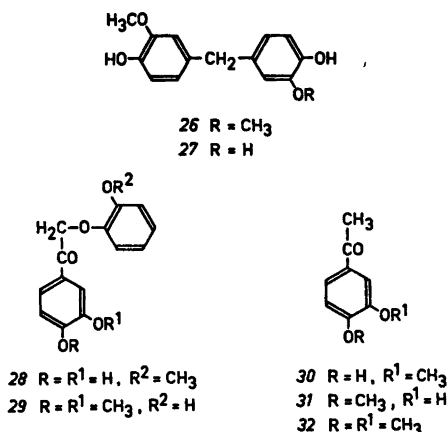


*Scheme 3.* Neutral sulfonation of 1-(3,4-dimethoxyphenyl)-2-guaiacoxy-3-hydroxypropane-1-one (*18*).

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*.[13] The latter adds bisulfite affording the keto sulfonic acid *21* which, by a $\beta$-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 *24*. The latter reaction step was demonstrated by treating authentic *24* with neutral sulfite and isolating *25* in high yield.[14]

It has previously [5] been reported that compound *18*, when treated with a sulfite solution of pH 6 at 135 °C for 5 h, gives a fair yield of the corresponding keto sulfonic acid (*21*, with $R^1$ instead of R). 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 $R^1$ 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, ω-guaiacoxyacetoguaiacone (*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 acetoveratrone (*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*.



*26* R = CH₃
*27* R = H

*28* R = R¹ = H, R² = CH₃
*29* R = R¹ = CH₃, R² = H

*30* R = H, R¹ = CH₃
*31* R = CH₃, R¹ = H
*32* R = R¹ = CH₃

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 *36*. 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 creosol 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 methane-sulfonic 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.
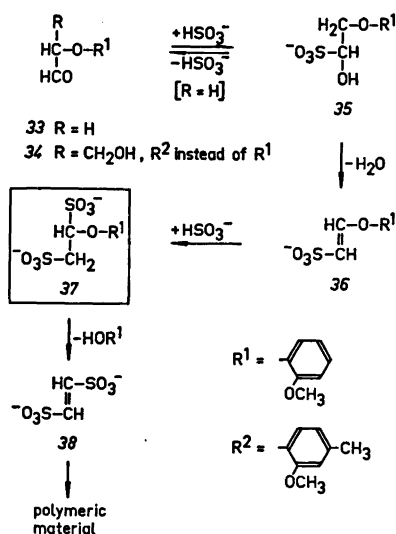
*Scheme 4.* Neutral sulfonation of guaiacoxy-acetaldehyde (*33*).

## CONCLUSIONS

All carbonyl-containing structural elements investigated here undergo sulfonation when subjected to the conditions of neutral sulfite pulping. In the case of structures A (coniferaldehyde end groups), the reaction sequences involved lead to the formation of carbonyl-free sulfonic acids and thus remove conjugated (chromophoric) systems (*cf.* also Ref. 1). Structures B (phenacyl aryl ether structures) afford phenacylsulfonic acids and other keto sulfonic acids with a concomitant cleavage of the phenacyl aryl ether linkage by β-elimination, sulfitolysis or reduction. This cleavage implies separation of two adjacent lignin units (fragmentation). Structures C ("detached" glyceraldehyde end groups) give a similar cleavage of the aryl alkyl ether bond accompanied by extensive polymerization of the liberated sulfonated aliphatic moiety.

All three types of carbonyl structures (A, B and C) undergo extensive sulfitolytic demethylation with formation of methanesulfonic acid. This reaction may give rise to catechol groups which are potential chromophores. The elimination of chromophoric groups by sulfite-addition to carbonyl-containing lignin structures (see above) may thus be counteracted by the

generation of potential chromophores of the catechol type. An analogous behaviour has recently [1] 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: *1*,[16] *6*,[17] *13*,[16] *18*,[5] *33*,[18] *34*.[19]*

*Sulfite treatment, work-up procedure, chromatographic, ¹H NMR and MS methods* have been previously described.[20,15]

*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: δ 6.6 − 7.9), methoxyl protons (ester and ether) (range: δ 3.5 − 3.9), aliphatic protons (range: δ 2.6 − 5.9) and acetoxyl protons (aromatically bound: δ 2.25 − 2.32, aliphatically bound: δ 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 keten (− 42) from aromatic acetyl groups, of ·SO₂OCH₃ (− 95) or HSO₂OCH₃ (− 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 Drs. Tapio Hase, Leila Lahtinen and Aarno Klemola, Helsinki, Finland, following an improved synthetic procedure (see *Acta Chem. Scand. B 31* (1977) 501), and kindly put at our disposal.

*Table 1.* Treatment of model compounds containing carbonyl groups with sulfite solutions.[a]

| Compound (mg) | Conditions | Products (mg) | |
|---|---|---|---|
| | | Chloroform-ether extract | Sulfonic acids, isolated as (acetylated) methyl esters |
| *1* (500) | NS | (60); SM, P | (525); *5* (155), *8* (290) (m.p. 74.5–75.0°) *12* (80), MSA+some P |
| *1* (1000) | AS | (60); P | (920) [b] |
| *13* (500) | NS | (60); V, VE | (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°), *17* (60), MSA |
| *18* (1000) | NS | (450); G (250), C (25), *24* (35), *26*+*30* (65),[b] *27*+*28*+*29* (40),[b] *31*+*32* (25) [b] | (1500); *22* (220) (m.p. 107.5–108.0°), *25* (350), MSA |
| *18* (500) | AS | (375); SM | Methylated *21* (150) |
| *33* (2000) | NS | (1040); G, C | (1720); *37* (260), MSA (290), P |
| *34* (1000) | NS | (665); Cr, MC | MSA, P |

[a] *Abbreviations.* Conditions: NS, treatment with neutral sulfite (pH 7) at 180 °C for 3 h. AS, treatment with acidic sulfite (pH 1.5) at 135 °C for 7 h. Products: C, catechol; Cr, creosol; G, guaiacol; MC, 4-methylcatechol; MSA, methanesulfonic acid; P, polymeric material; SM, starting material; V, vanillin; VE, veratraldehyde. [b] The components were indentified by MS without complete separation from each other.

identified by the ¹H NMR (60 MHz, CDCl₃) and mass spectral data given.

(1) *After neutral sulfonation (pH 7, 180 °C, 3 h) From compund 1:**
1-(4-Acetoxy-3-methoxyphenyl)-3-acetoxypropane-1-sulfonic acid methyl ester (methyl ester of *5*-diacetate). ¹H NMR: δ 1.98 (s, 3 H, Ac), 2.29 (s, 3 H, Ac), 2.6 (broad s, 2 H, CH₂), 3.67 (s, 3 H, OMe), 3.84 (s, 3 H, OMe), 4.2 (broad s, 3 H, CH+CH₂), 7.00 (3 H, ar). MS *m/e* (rel. int.): 360 (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*-acetate). m.p. 74.5–75.0 °C. ¹H NMR: δ 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), 151 (M − 42 − 95, 100), 150 (M − 42 − 96, 27).
5,6-Diacetoxyindane-1,3-disulfonic acid diethyl ester (dimethyl ester of *12*-diacetate). ¹H NMR: δ 2.27 (s, 6 H, Ac), 3.09 (2 H, CH₂), 3.82 (s, 6 H 2×OMe), 4.92 (2 H, 2×CH),

7.51 (2 H, ar). MS *m/e* (rel. int.): 422 (M 3), 380 (M − 42, 28), 338 (M − 2 × 42, 41), 285 (M − 42 − 95, 83), 243 (M − 42 − 95, 100), 242 (M − 2 × 42 − 96, 8), 190 (M − 42 − 2 × 95, 4), 189 (M − 42 − 95 − 96, 34), 148 (M − 2 × 42 − 2 × 95, 10), 147 (M − 2 × 42 − 95 − 96, 48).
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*-acetate). ¹H NMR: δ 2.13 (s, 3 H, Ac), 2.96 (broad s, 2 H, CH₂), 3.67 (s, 3 H, OMe), 3.87 (9 H, 3×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), 331 (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*-diacetate). 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-propene-1,3-disulfonic acid dimethyl ester (dimethyl ester of demethylated and dehydrated *14*-acetate).

* All compounds investigated here gave methanesulfonic acid methyl ester in addition to the sulfonic acid esters mentioned.

MS $m/e$ (rel.int.): 394 (M, 2), 352 (M − 42, 7), 257 (M − 42 − 95, 22), 161 (M − 42 − 95 − 96, 100).

*3-(3,4-Dimethoxyphenyl)-3-methoxysulfonyl-propionic acid methyl ester* (dimethyl ester of *16*). m.p. 94.5 − 96.5°. $^1$H NMR: $\delta$ 3.29 (d, 2 H, CH$_2$), 3.62 (s, 3 H, OMe), 3.69 (s, 3 H, OMe), 3.87 (6 H, 2 × OMe), 4.73 (1 H, CH), 6.91 (3 H, ar). IR (KBr): 1725 (s, C=O) cm$^{-1}$. MS $m/e$ (rel. int.): 318 (M, 13), 223 (M − 95, 100), 222 (M − 96, 19), 191 (M − 96 − 31, 10), 181 (M − 137, 80), 164 (M − 95 − 59, 10).

*1-(3,4-Dimethoxyphenyl)-3-acetoxypropane-1-sulfonic acid methyl ester* (methyl ester of *17*-acetate). $^1$H NMR: $\delta$ 1.98 (s, 3 H, Ac), 2.6 (broad s, 2 H, CH$_2$), 3.67 (s. 3 H, OMe), 3.84 (6 H, 2 × OMe), 4.2 (broad s, 3 H, CH + CH$_2$), 6.89 (3 H, ar). MS $m/e$ (rel. int.): 332 (M, 9), 237 (M − 95, 2), 177 (M − 95 − 60, 100).

*From compound 18:*

*1-(4-Acetoxy-3-methoxybenzoyl)ethene-2-sulfonic acid methyl ester* (methyl ester of *22*-acetate). $^1$H NMR: $\delta$ 2.32 (s, 3 H, Ac), 3.89 (6 H, 2 × OMe), 7.19 (d, 1 H, ol, $J$ 15.3 Hz), 7.24 (1 H, ar), 7.67 (2 H, ar), 7.84 (d, 1 H, ol, $J$ = 15.3 Hz). IR (KBr): 1660 (s. C=C−C=O) cm$^{-1}$. MS $m/e$ (rel. int.): 314 (M, 9), 272 (M − 42, 100), 177 (M − 42 − 95, 24), 176 (M − 42 − 96, 22), 151 (M − 42 − 95 − 26, 53).

*4-Acetoxy-3-methoxyacetophenone-ω-sulfonic acid methyl ester* (methyl ester of *25*-acetate). $^1$H NMR: $\delta$ 2.30 (s, 3 H, Ac), 3.89 (s, 3 H, OMe), 3.96 (s, 3 H, OMe), 4.67 (s, 2 H, CH$_2$), 7.00 (1 H, ar), 7.56 (2 H, ar). MS $m/e$ (rel. int.): 302 (M, 6), 260 (M − 42, 89), 151 (M − 42 − 109, 100).

*From compound 33:*

*1-(2-Methoxyphenoxy)ethane-1,2-disulfonic acid dimethyl ester* (dimethyl ester of *37*). $^1$H NMR: $\delta$ 3.50 (s, 3 H, OMe), 3.69 (s, 3 H, OMe), 3.76 (s, 3 H, OMe), 4.1 − 4.8 (broad s, 3 H, CH + CH$_2$), 6.6 − 7.1 (broad s, 4 H, ar). MS $m/e$ (rel. int.): 340 (M, 33), 245 (M − 95, 100), 244 (M − 96, 28), 150 (M − 2 × 95, 80), 149 (M − 95 − 96, 22), 148 (M − 2 × 96, 23), 124 (32).

(2) *After acidic sulfonation (pH 1.5, 135 °C, 7 h)*

*From compound 1:*

*3-(4-Acetoxy-3-methoxyphenyl)propionic aldehyde-3-sulfonic acid methyl ester* (methyl ester of *3*-acetate). MS $m/e$ (rel.int.): 221 (M − 95, 2), 220 (M − 96, 7), 179 (M − 42 − 95, 13), 178 (M − 42 − 96, 100).

*From compound 18:*

*1-(3,4-Dimethoxyphenylbenzoyl)-1-(2-methox-yphenoxy)ethane-2-sulfonic acid methyl ester* (methyl ester of methylated *21*). $^1$H NMR: $\delta$ 3.73 (s, 3 H, OMe), 3.84 (s, 3 H, OMe), 3.87 (s, 3 H, OMe), 3.89 (s, 3 H, OMe), 4.22 (d, 2 H, CH$_2$), 5.96 (tr, 1 H, CH), 6.89 (5 H, ar), 7.60 (2 H, ar). MS $m/e$ (rel. int.): 410 (M, 7), 315 (M − 95, 5), 314 (M − 96, 20), 192 (M − 95 − 123, 8), 165 (M − 245, 100), 150 (M − 245 − 15), 124 (22).

From the chloroform-ether soluble fractions after the neutral sulfonations, the following

compounds were isolated by TLC or LC (phenolic compounds as acetates) and identified by $^1$H NMR and/or GC-MS (comparison with authentic samples, if available): guaiacol, creosol, catechol, 4-methylcatechol, vanillin and veratraldehyde as well as compounds *24* and *26 − 32*.

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