

The Reactions of Lignin during Neutral Sulfite Pulping. Part V.*

The Reactions of α -(4-Hydroxy-3-methoxyphenyl)-glycerol- β -guaiacyl Ether with Sulfite and their Dependence on pH**

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Dedicated to Professor Dr. Karl Kratzl on the occasion of his 60th birthday.

The sulfonation of the phenolic arylglycerol- β -aryl ether units in lignin at different pH values has been studied using a model compound (I, Scheme 1).

The primary product, the quinonemethide II, undergoes three competing reactions:

(1) nucleophilic addition of sulfite; (2) elimination of the terminal hydroxymethyl group as formaldehyde; (3) elimination of water.

Sulfonic acid groups may be introduced in all positions of the (substituted) glycerol side chain since the conjugated products formed in reactions 2 and 3 add hydrogen sulfite (and/or sulfite) ions giving rise to α - and γ -sulfonic acids and the β -aryl ether bond may be sulfitolitically cleaved giving β -sulfonic acids.

The α -sulfonic acid group of the α , β -disulfonic acids may be eliminated as bisulfite with formation of styrene- β -sulfonic acids. When the pH of the sulfite reaction is increased, this elimination and reactions 2 and 3 become more important.

Guaiacol formed in the sulfite treatment of I condenses with the hydroxymethanesulfonic acid (sulfomethylation, Scheme 2) that is formed by addition of sulfite to the formaldehyde produced in reaction 2. Guaiacol also adds to styrene- β -sulfonic acids affording 1,1-diarylethane- and 1,1-diarylpropane sulfonic acids.

The formation of the different sulfonic acids can be accounted for by the reaction sequences outlined in Schemes 1 and 2. The significance of these reactions for lignin sulfonation is discussed briefly.

* Part IV, see Ref. 14.

** Preliminary reports on the results of this work have been given (by J. G.) at the International Sulfite Pulping and Recovery Conference in Boston, Mass., October 30—November 3, 1972. Abstr. of Papers, p. 323 and at the Annual Meeting of Zellcheming in Baden-Baden, West Germany, June 25—30, 1973.

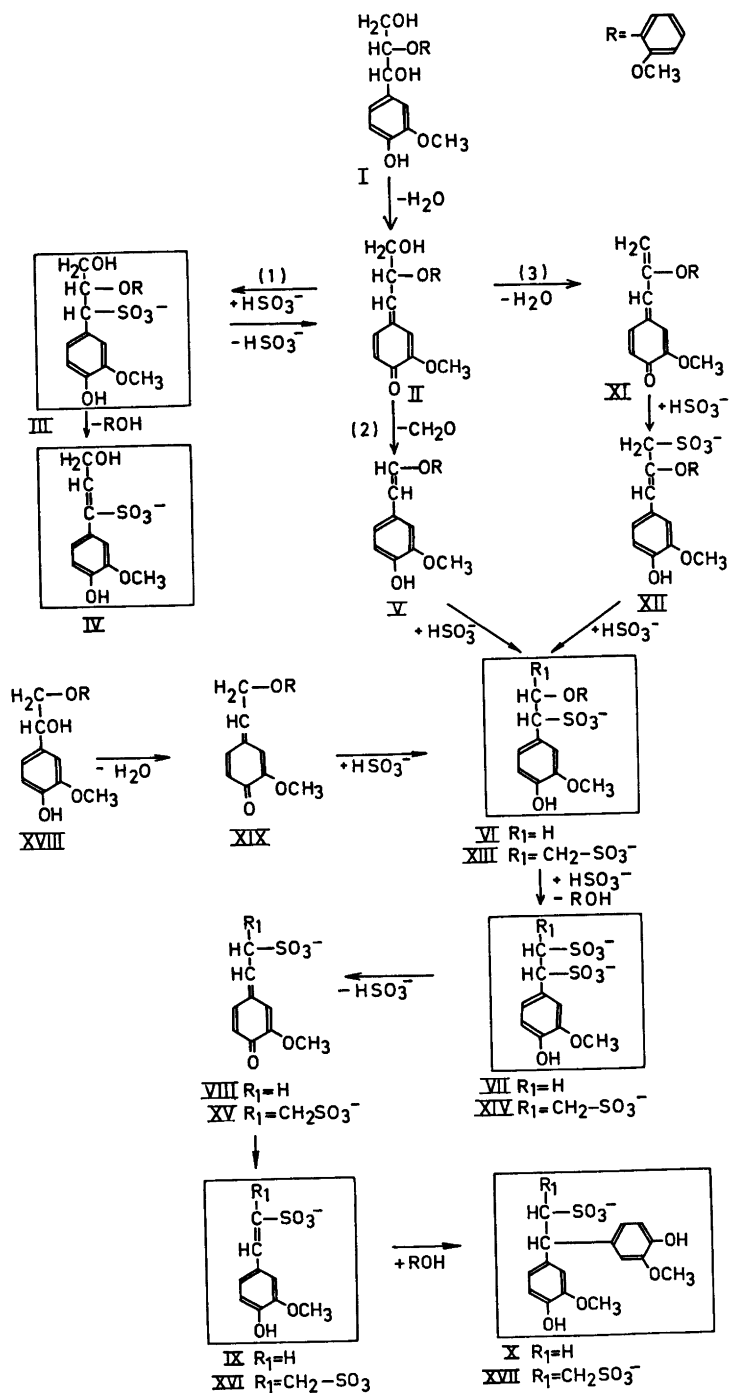
Previous communications in this series have described the reactions of the phenolic β -aryl ether units of lignin with sulfite under acidic and neutral conditions.

Model compound I, when treated with sulfite solution at pH 1.5 gives a mixture of *erythro*- and *threo*-forms of the corresponding α -sulfonic acid (III).¹ When the simpler model compound XVIII is treated with neutral sulfite solution and the pH is allowed to rise to 10 during the reaction, the main product is the styrene- β -sulfonic acid IX.² This reaction apparently proceeds *via* α -sulfonation, sulfitolitic cleavage of the β -guaiacyl ether bond of the α -sulfonic acid (VI) giving the α , β -disulfonic acid VII, and then elimination of bisulfite to form the corresponding styrene- β -sulfonic acid.³

In the present work the reaction of β -aryl ether type structural elements with sulfite at different pH values were reinvestigated using I as a model substance.

RESULTS AND DISCUSSION

Compound I was treated with sulfite solution at different pH values (and at 180 °C unless otherwise indicated). Due to the liberation of hydroxyl and alkoxy ions in the sulfonation process, the pH of the solution increases unless a sufficiently large excess of sulfite is used. The reaction mixtures, on working up as described previously,¹ give a chloroform-ether soluble fraction containing varying amounts of guaiacol and catechol but no starting material, and a water-



Scheme 1. Sulfonic acids are given as anions. Compounds isolated (in the form of acetylated sulfonic acid methyl esters) are shown in frames.

Table 1. Treatment of compound I with sulfite solutions of different pH values.

pH	4.0	7.0	7.0	7.0-8.5	9.5-11.0
Temperature, °C	155	180	180	180	180
Time, h	4	3	6	3	3
Amount of I, g	1.0	3.0	2.0	3.0	4.0
Amount of sulfite solution, ml	80	240	160	160	160
Solvent system	A	A	A	B	A→C, gradient elution
Phenols, mg	traces	375	480	510	853
Compound ^a					
III (<i>erythro</i> and <i>threo</i>)	* ^{b,c}	*	+	*	
IV		+ ^d	(+)	+	+
VII		+	*	+	+
IX			(+)		+
X				(+)	+
XIII				(+)	
XIV					+
XVI			+		
XVII					+
XXII		+	+	+	+
XXIII		+	+	+	+
XXIV			+		+
XXV			+		
MS		+	+	+	+
Total yield, g	1.75	3.25	2.25	4.0	

^a Acetylated methyl ester of the corresponding sulfonic acid. ^b +, present; (+), small amount or traces; *, main product. ^c *erythro-threo* 2:1. ^d M.p. 96-98 °C.

soluble fraction containing sulfonic acids. The latter were converted into acetylated methyl esters,¹ and after separation by column chromatography these were identified by NMR and mass spectrometry.

Table 1 shows the sulfonic acids obtained in the treatments at different pH values. Tentative routes for their formation are outlined in Schemes 1 and 2.

Treatment at pH 4, 155 °C (4 h). The simplest reaction mixture was obtained by treatment with a weakly acidic sulfite solution of pH 4. As in the reaction at pH 1.5,¹ the *erythro* and *threo* forms of the α -sulfonic acid III* were formed in a ratio of approximately 2:1. This was independent of the diastereoisomeric form of the starting β -aryl ether (I), supporting the view that α -sulfonation proceeds by a S_N1 mechanism *via* a common intermediate, the quinone-methide II (pathway 1), and/or the benzylium ion derived from I.¹ To give further support for

this interpretation, a solution of the quinone-methide II was prepared from compound I and treated with neutral sulfite solution at room temperature. Both stereoisomeric forms of the α -sulfonic acid III were isolated, the *erythro* form being the major component.

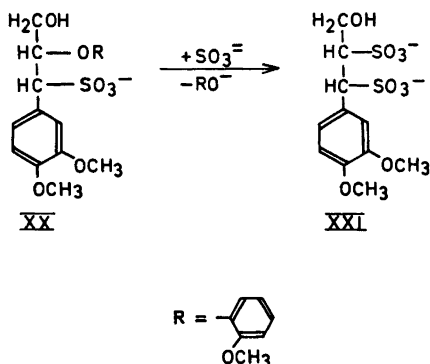
Treatment at pH 7 (3 h). When the pH of the sulfite treatment was raised from 4.0 to 7.0, the *erythro*- and *threo*-forms of the α -sulfonic acid III were still the main products but the sulfonation mixture also contained the sulfonic acids IV, VII, XXII, and XXIII, as well as methane-sulfonic acid.

The styrene- β -sulfonic acid derivative IV which was obtained in a small amount apparently arises by elimination of guaiacol from III (β -elimination). It has been previously^{4,5} suggested as an intermediate in the alkali-promoted formation of acetoguaiacone and formaldehyde from III.

The α,β -disulfonic acid VII can obviously be formed by elimination of formaldehyde from the intermediate quinonemethide II (reverse aldol reaction⁶), followed by addition of bisulfite to the resulting β -guaiacoxystyrene derivative V (formation of the α -sulfonic acid VI) and then

* For the sake of uniformity the side chain carbon atoms are denoted by α , β , and γ (starting from the carbon atom adjacent to the aromatic nucleus) throughout the general part of this work. For systematic nomenclature, see experimental section.

by sulfitolytic cleavage of the β -guaiacyl ether bond in VI [route (2), *cf.* also Ref. 2]. Support for this suggested route was obtained by isolation of the α -sulfonic acid VI and the α,β -disulfonic acid VII in yields of 20 and 70 %, respectively, after treatment of the β -guaiacyl ether XVIII with sulfite under the same conditions. The sulfonic acids VI and VII could arise by addition of bisulfite either to the intermediate quinonemethide XIX⁸ or to the intermediate β -guaiacoxystyrene derivative V (see above). The sulfitolytic cleavage of a β -guaiacyl ether bond was demonstrated using the non-phenolic α -sulfonic acid XX. The corresponding α,β -disulfonic acid (XXI) was isolated in the diastereoisomeric forms with a ratio of *threo*- to *erythro*-forms of approximately 2:1.



The benzylsulfonic acids XXII and XXIII are formed by condensation of guaiacol either with hydroxymethanesulfonic acid (sulfomethylation, Scheme 2) or with formaldehyde followed by sulfonation of the resulting *ortho*- and *para*-hydroxybenzyl alcohols. Guaiacol is liberated by sulfitolytic cleavage of the β -arylether linkage and hydroxymethanesulfonic acid is generated by reaction of bisulfite with formaldehyde, eliminated from the quinonemethide II (Scheme 1, route 2). In agreement with this interpretation, the benzylsulfonic acids XXII and XXIII (and the disulfonic acid XXIV) were obtained when guaiacol was treated with neutral sulfite in the presence of formaldehyde under similar conditions. (For the condensation of hydroxymethanesulfonic acid with phenol, see Ref. 7.)

The sulfomethylation of guaiacol is reminiscent of the condensation reactions taking place in alkali and sulfate pulping in which formalde-

hyde reacts with phenolic structural units to give benzyl alcohol- and then diarylmethane structures.⁹⁻¹¹ In the present instance, the formation of diarylmethane derivatives is prevented by the reaction of formaldehyde or the benzyl alcohol intermediates with bisulfite.

The aliphatic degradation product methane-sulfonic acid arises by sulfitolytic cleavage of methyl aryl ether bonds as described previously^{2,3,12} (*cf.* also formation of catechol and XXV).

Treatment at pH 7 (6 h). Prolongation of the sulfite treatment at pH 7 from 3 to 6 h resulted in the formation of 4 additional sulfonic acids.

A small amount of the styrene- β -sulfonic acid derivative IX was formed by elimination of bisulfite from the α,β -disulfonic acid VII. The sulfonic acid IX was also obtained, together with the disulfonic acid VII, when compounds XVIII⁸ or V were treated in the same way (Scheme 1).

An analogous elimination of bisulfite from the α,β,γ -trisulfonic acid XIV (see below) gave rise to the formation of the styrene- β -sulfonic acid derivative XVI.

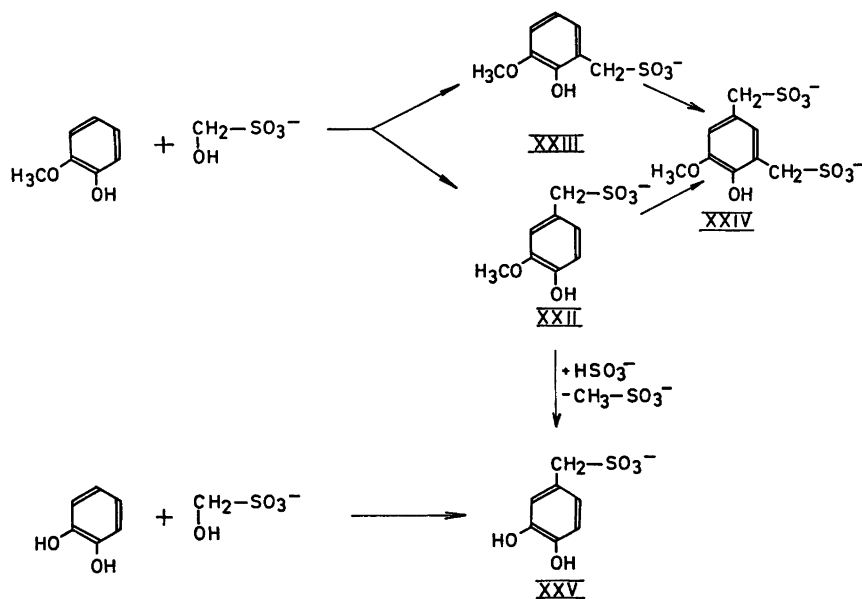
The benzylsulfonic acids XXIV and XXV were produced by sulfomethylation of XXII, XXIII, and catechol, respectively. Compound XXV could also arise from XXII by sulfitolytic demethylation.

Treatment at pH 7.0–8.5 (3 h). When compound I was treated with a sulfite solution containing reduced amounts of sodium sulfite, the pH increased during the reaction from 7.0 to 8.5. In addition to the sulfonic acids obtained on sulfonation at a constant pH of 7.0 (3 h), the reaction mixture contained small amounts of two sulfonic acids:

The β -sulfonic acid X arises by the reaction of the α,β -disulfonic acid VII with guaiacol, as was shown in a separate experiment. The quinonemethide- β -sulfonic acid VIII and the styrene- β -sulfonic acid derivative IX are possible intermediates.

The α,γ -disulfonic acid XIII is formed on a route which is described in connection with the formation of the sulfonic acids XIV, XVI, and XVII (see below).

Treatment at pH 9.5–11.0 (3 h). The resulting reaction mixture contained disulfonic acid VII, the styrene- β -sulfonic acid derivative IX, β -sulfonic acid X, and benzylsulfonic acids



Scheme 2.

XXII–XXIV as major components. Small amounts of the styrene- α -sulfonic acid derivative IV, the α,β,γ -trisulfonic acid XIV, the styrene- β -sulfonic acid derivative XVI, and the β,γ -disulfonic acid XVII were also isolated.

The formation of the α,γ - and β,γ -disulfonic acids [XIII (see above) and XVI, XVII, respectively], and of the α,β,γ -trisulfonic acid XIV, can be accounted for as follows:

The intermediate quinonemethide II, on elimination of water, will give the extended quinonemethide XI, route 3, which will afford the α,γ -disulfonic acid XIII by 1,8- and then 1,2-addition of bisulfite. This reaction sequence is analogous to the sulfonations of coniferyl alcohol^{13,14} and of pinoresinol¹⁴ in neutral and alkaline solutions. It has been suggested recently¹⁴ that these reactions also proceed *via* extended quinonemethides. Sulfolytic cleavage of the β -aryl ether bond in XIII can afford the α,β,γ -trisulfonic acid XIV and this, probably *via* the quinonemethide XV, can yield the styrene- β -sulfonic acid derivative XVI. Addition of guaiacol to XVI will then give the β,γ -disulfonic acid XVII.

The α -sulfonic acid III, the main sulfonation

product formed at lower pH-values, was absent. This finding may be explained by the competition of the elimination reactions 2 and 3 with the sulfite addition reaction 1 (Scheme 1) and by the reversibility of the latter. Treatment of the α -sulfonic acid III with a sulfite solution of pH 9.5 under similar conditions yielded small amounts of the disulfonic acid VII together with other sulfonic acids. The α -sulfonic acid III which might be formed at higher pH is likely to be consumed by the elimination reaction affording the styrene- α -sulfonic acid derivative IV.

SUMMARY AND CONCLUSIONS

Formation of the sulfonic acids shown in Scheme 1 proceeds *via* a common intermediate, the quinonemethide II, which may undergo three alternative conversions:

(1) Addition of bisulfite to give the α -sulfonic acid III. Elimination of guaiacol can then yield the styrene- α -sulfonic acid derivative IV.

(2) Elimination of formaldehyde to form the β -guaiacoxystyrene derivative V. Subsequent addition of bisulfite, sulfolytic cleavage of the

β -guaiacyl ether bond, elimination of bisulfite and addition of eliminated guaiacol will convert the intermediate V into the sulfonic acids VI, VII, IX, and X.

(3) Elimination of water to form the extended quinonemethide XI and, by 1,8-addition of bisulfite, the β -guaiacoxystyrene derivative XII. The subsequent reactions of this intermediate, including 1,2-addition of bisulfite, sulfolytic cleavage of the β -guaiacyl ether linkage, elimination of bisulfite and addition of guaiacol are analogous to those of the β -guaiacoxystyrene derivative V and will give the sulfonic acids XIII, XIV, XVI and XVII.

The formaldehyde eliminated in reaction (2) and bisulfite, or the formaldehyde-bisulfite addition product (hydroxymethanesulfonic acid), will condense with guaiacol or with catechol to afford the benzylsulfonic acids XXII–XXV (Scheme 2).

The relative importance of the three pathways outlined in Scheme 1 and the sulfomethylation reactions outlined in Scheme 2 will be dependent on the reaction conditions used. The pH during the sulfite treatment appears to have a decisive effect on the course of the sulfonation and, thus, on the qualitative and quantitative composition of the final mixture of sulfonic acids. Another important factor seems to be the length of the sulfite treatment.

Although some of the sulfonic acids expected were not isolated as the methyl esters because of separation difficulties in the column chromatography, some general features of the reactions of compound I in sulfite solutions of different pH values can be discerned.

In the pH-range 4 to 8.5 the nucleophilic addition of sulfite to II (pathway 1) is the main reaction. At about pH 7 the elimination pathway 2 and, at a somewhat higher pH, pathway 3 become more and more competitive and predominate at pH values higher than about 9.5. This is reflected by the increased formation of guaiacol and catechol and by the larger amounts of condensation products formed from these phenols and hydroxymethanesulfonic acid or conjugated intermediates. These changes in the reaction patterns of compound I with sulfite solutions are gradual and no distinct pH-limits for the various routes and reaction steps can be drawn.

The finding that all three types of carbon atoms of the side chains (α , β , and γ) in phenolic β -aryl ether structures may be involved in the sulfonation of lignin is in agreement with previous analytical studies.¹⁵ Reactions at these sites and sulfomethylation reactions have to be taken into account, if the reactive groupings in lignin are to be correctly classified into categories according to their ease of sulfonation (cf. Ref. 16).

EXPERIMENTAL

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

Thin-layer and column chromatography. Phenols and sulfonic acid esters were separated on an analytical scale by TLC using silica gel HF₂₅₄, the solvent systems used unless otherwise stated were: phenols: chloroform-acetone 4:1; sulfonic acid esters: cyclohexane-ethyl acetate 1:1 (A), 3:2 (B), and 7:3 (C). Preparative separations were carried out with a liquid chromatograph (Chromatronix Inc., Berkeley, California) using silicic acid (Bio-Sil A, 20–44 μ , Bio-Rad Laboratories, Richmond, California) as the stationary phase and the same solvent systems as in the analytical separations. The flow rate in a 12.7 \times 1000 mm column was 1 ml/min and the pressure approximately 170 kPa.

NMR spectrometry. NMR spectra (CDCl₃) were recorded with a Perkin-Elmer R-12 spectrometer. The NMR-data are summarized in Table 2. Chemical shifts (δ -values) are given in ppm downfield from TMS.

Mass spectrometry. Mass spectra were recorded on a Perkin-Elmer 270 instrument at 20 eV using the direct inlet system. The temperature of the probe heater was 50 °C. Mass spectral data are summarized in Table 3.

Model compounds. The model compounds used were prepared as previously described (references are given below).

Sulfite solutions (a) pH 4, Na₂S₂O₅ (0.25 mol) in distilled water (1 l); (b) pH 7, Na₂S₂O₅ (0.25 mol) in distilled water (1 l) was adjusted to pH 7 with 2 N NaOH; (c) pH 9, Na₂SO₃ (0.5 mol) in distilled water (1 l).

Sulfite treatment. The model compound, suspended in the sulfite solution, was heated under pressure at 180 °C for 3 h unless otherwise stated.

Work-up procedure. The work-up procedure has been previously described.¹ The mixtures of chloroform-ether soluble compounds consisted of guaiacol and catechol only. The sulfonic acids in the aqueous solutions were converted to acetylated sulfonic acid methyl esters. These mixtures were investigated by TLC and then separated by repeated preparative column chromatography into several fractions. Yields of the chro-

Table 2. Proton chemical shifts (δ -values) of acetylated sulfonic acid methyl esters.

Compound acetylated methyl ester of	Aromatic, olefinic H	Aliphatic H	OCH ₃ (ester, ether)	Acetyl H	
				Aromatic	Aliphatic
IV	6.8-7.1 (m, 4 H)	4.62 (d, 2 H _{γ}) ^a	3.80 (s, 3 H) 3.71 (s, 3 H)	2.28 (s, 3 H)	2.00 (s, 3 H)
X	6.7-7.0 (m, 6 H)	3.78 (d, 2 H β) 4.53 (t, 1 H α) ^b	3.49 (s, 3 H) 3.74 (s, 6 H)	2.23 (s, 6 H)	
XIV	6.8-7.2 (m, 3 H)	3.4-4.1 (4 H) ^c	3.71 (s, 3 H) 3.77 (s, 3 H) 3.80 (s, 3 H) 3.82 (s, 3 H) 3.89 (s, 3 H)	2.30 (s, 3 H)	
XVII	6.7-7.1 (m, 6 H)	3.4-4.1 (4 H) ^c	3.51 (s, 3 H) 3.64 (s, 3 H) 3.74 (s, 6 H)	2.24 (s, 3 H) 2.27 (s, 3 H)	
XXI (erythro)	6.8-7.0 (m, 3 H)	4.00-4.30 (m, H β) 4.75-5.00 (H α +2 H γ)	3.48 (s, 3 H) 3.61 (s, 3 H) 3.86 (s, 3 H)		2.12 (s, 3 H)
XXI (threo)	6.85-7.10 (m, 3 H)	loc. uncertain	3.61 (s, 3 H) 3.74 (s, 3 H) 3.87 (s, 3 H)		1.96 (s, 3 H)
XXII	6.98 (s, 3 H)	4.28 (s, 2 H)	3.74 (s, 3 H) 3.80 (s, 3 H)	2.28 (s, 3 H)	
XXIII	6.9-7.3 (m, 3 H)	4.32 (s, 2 H)	3.72 (s, 3 H) 3.80 (s, 3 H)	2.30 (s, 3 H)	
XXIV	7.0-7.2 (broad s, 3 H)	4.31 (s, 4 H)	3.73 (s, 3 H) 3.80 (s, 3 H) 3.82 (s, 3 H)	2.32 (s, 3 H)	

^a $J_{\beta\gamma}$ 6.0 Hz. ^b $J_{\alpha\beta}$ 6.7 Hz. ^c Location of aliphatic H uncertain due to overlapping of OCH₃.

Table 3. Mass spectral fragmentation of acetylated sulfonic acid methyl esters (all fragments having $m/e > 130$ and intensities $> 5\%$ of the base peak are accounted for).

Compound, acetylated methyl ester of	M (m/e)	M - $n \times 42^a$ ($n = 0, 1, 2$)	M - $n \times 42$ - 95/96 ^b	M - $n \times 42$ - $2 \times 95/96$	M - $n \times 42$ - $3 \times 95/96$	Misc.
IV	358 (11)	316 (100)	221 (21) 220 (64)			205 (37) 192 (16) 179 (83)
VII	382 (1)	340 (5)	245 (41) 244 (12)	150 (100) 149 (10) 148 (21)		
IX	286 (4)	244 (100)	149 (20) 148 (85)			
X	452 (4)	410 (32) 368 (60)	273 (21) 272 (100)			259 (35)
XIII	518	476				352 } 257 } ^c 161 }
XIV	490 (3)	448 (17)	353 (72) 352 (16)	258 (24) 257 (36)	163 (19) 162 (6) 161 (19)	
XVI	394 (6)	352 (100)	257 (34)	161 (49)		255 (50) 193 (22) 178 (22)
XVII	560 (3)	518 (28) 476 (61)	381 (16) 380 (43)	285 (7) 284 (9)		353 (8) 259 (11) 257 (10) 163 (22) 149 (100)
XXI (<i>erythro</i>) ^d	426 (20)		331 (13) 330 (6)	236 (16)		271 (100) 193 (15) 176 (8) 175 (25)
XXII	274 (3)	232 (18)	137 (100) 136 (14)			
XXIII	274 (5)	232 (82)	137 (100) 136 (80)			
XXIV	382 (8)	340 (45)	245 (100)	149 (18)		
XXV	302 (4)	260 (32) 218 (100)	123 (38) 122 (55)			

^a $m/e = 42$ corresponds to CH_2CO arising from aromatic acetyl groups. ^b $m/e = 95$ and 96 corresponds to $\cdot\text{SO}_3\text{OCH}_3$ and HSO_3OCH_3 , respectively. ^c $\text{M} - 42 - 124 - n \times 95/96$ ($n = 0, 1, 2$) ^d The *threo*-form afforded the same fragments but with different intensities.

matographic fractions were not determined since this purification procedure involved considerable losses of material. Unless otherwise stated, the acetylated sulfonic acid methyl esters were obtained as colourless amorphous substances. Many of them decomposed rapidly, even when kept at low temperature (about 2 °C).

Treatment of compound I with sulfite solutions

Table 1 summarises the results from the treatments of compound I¹⁷ with sulfite solutions under different conditions.

The following acetylated sulfonic acid methyl esters were isolated (Table 1) and identified by NMR and mass spectrometry (Tables 2 and 3, respectively) and/or by comparison of the spectra with those of authentic samples:

erythro- and threo-1-(4-Acetoxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-3-acetoxypropane-1-sulfonic acid methyl ester (methyl esters of erythro and threo-III-diacetate).

α -Methoxysulfonyl- β -acetoxyethyl-4-acetoxy-3-methoxystyrene (methyl ester of IV-diacetate).

1-(4-Acetoxy-3-methoxyphenyl)-ethane-1,2-disulfonic acid dimethyl ester (dimethyl ester of VII-acetate).

trans-4-Acetoxy-3-methoxystyrene- β -sulfonic acid methyl ester (methyl ester of trans-IX-acetate)

1,1-Bis(4-acetoxy-3-methoxyphenyl)ethane-2-sulfonic acid methyl ester (methyl ester of X-diacetate).

1-(4-Acetoxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-disulfonic acid dimethyl ester (dimethyl ester of XIII-acetate).

1-(4-Acetoxy-3-methoxyphenyl)propane-1,2,3-trisulfonic acid trimethyl ester (trimethyl ester of XIV-acetate).

β -Methoxysulfonylmethyl- β -methoxysulfonyl-4-acetoxy-3-methoxystyrene (dimethyl ester of XVI-acetate).

1,1-Bis(4-acetoxy-3-methoxyphenyl)propane-2,3-disulfonic acid dimethyl ester (dimethyl ester of XVII-diacetate).

4-Acetoxy-3-methoxybenzylsulfonic acid methyl ester (methyl ester of XXII-acetate).

2-Acetoxy-3-methoxybenzylsulfonic acid methyl ester (methyl ester of XXIII-acetate).

4-Acetoxy-3-methoxy-1,5-di(methoxysulfonylmethyl)benzene (dimethyl ester of XXIV-acetate).

3,4-Diacetoxybenzylsulfonic acid methyl ester (methyl ester of XXV-diacetate).

Methanesulfonic acid methyl ester.

Treatment of quinonemethide II with neutral sulfite at room temperature

Quinonemethide II, dissolved in chloroform, was prepared from compound I and treated with

neutral sulfite solution as described previously³ for compound XIX. The remaining chloroform solution contained small amounts of starting material and of three other components, which were not characterised. The mixture of acetylated sulfonic acid methyl esters obtained from the aqueous solution following the usual working-up procedure contained, according to TLC (Solvent system B) the erythro and threo-forms of the methyl ester of III-diacetate, with the erythro-form predominant.

Treatment of the α -sulfonic acid III with sulfite at pH 9.5 (3 h)

The methyl ester of III-diacetate (erythro-form)¹ (500 mg) was treated with sodium sulfite solution (18 ml). The reaction product contained the erythro and threo-forms of the starting compound (approximate ratio 2:1), together with small amounts of the dimethyl ester of VII-acetate (TLC and mass spectrometry). Traces of other components were detected by TLC but not identified.

Treatment of the α -sulfonic acid XX with neutral sulfite

The sodium salt of compound XX¹⁸ (800 mg, mixture of erythro- and threo-forms) was treated with neutral sulfite (80 ml); pH 7 before and after treatment. Preparative separation of the sulfonic acid esters using benzene-acetone (19:1) as the solvent system gave:

threo-1-(3,4-Dimethoxyphenyl)-3-acetoxypropane-1,2-disulfonic acid dimethyl ester (dimethyl ester of threo-XXI-acetate) (70 % of the isolated material); rapidly decomposing oil.

erythro-1-(3,4-Dimethoxyphenyl)-3-acetoxypropane 1,2-disulfonic acid dimethyl ester (dimethyl ester of erythro XXI-acetate) (30 % of the isolated material); recrystallized from ethanol; m.p. 119.5 – 120.0 °C.

Treatment of XVIII with neutral sulfite

Compound XVIII⁶ (1 g) was treated with neutral sulfite solution (80 ml); pH 7 before and after treatment. The chloroform-ether soluble fraction (190 mg) contained guaiacol and catechol. Preparative separation of the sulfonic acid esters using solvent system A gave: methyl ester of trans-IX-acetate (small amount), methanesulfonic acid methyl ester, 1-(4-acetoxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)ethane-1-sulfonic acid methyl ester (methyl ester of VI-acetate)² (20 % of the isolated material), and dimethyl ester of VII-acetate (70 % of the isolated material). The last-mentioned compound was identical with the product obtained from compound I.

Treatment of XVIII with sulfite at pH 9

Compound XVIII (1 g) was treated with the sulfite solution (80 ml) (pH 9 before and after treatment). The chloroform-ether soluble fraction (240 mg) contained guaiacol and catechol. Preparative separation of the sulfonic acid esters using solvent system A gave: methyl ester of *trans*-IX-acetate (43 % of the isolated material), identical with the corresponding product obtained from I, methanesulfonic acid methyl ester, dimethyl ester of VII-acetate (43 % of the isolated material) and methyl ester of X-diacetate (14 % of the isolated material), identical with the corresponding product obtained from I.

Treatment of the β -guaiacoxy-styrene derivative V with neutral sulfite

The sodium salt of compound V* (330 mg) was treated with neutral sulfite solution (18 ml). Catechol, guaiacol, and starting material were found in the chloroform-ether soluble fraction [TLC, chloroform-acetone (9:1)]. Paper chromatography of the aqueous solution [Whatman No. 3 paper; ethanol-conc. ammonia-water (12:1:3)] showed the presence of methanesulfonic acid and of the sulfonic acids VII and IX (co-chromatography of authentic samples).

Treatment of the disulfonic acid VII with guaiacol at pH 10

The disulfonic acid (VII)* (sodium salt, 50 mg) was treated with an excess of guaiacol in borate buffer (pH 10). Working-up of the aqueous solution gave the methyl ester of X-diacetate, identical with the product obtained from I and from XVIII (see Scheme 1).

Treatment of guaiacol with neutral sulfite (pH 8) in the presence of formaldehyde

Guaiacol (1.0 g, 8.07 mmol) was treated with a solution of neutral sulfite (80 ml, 40 mmol) and a 30 % formalin solution (3 ml) (pH 8 before and after treatment). The chloroform-ether extract (250 mg) contained starting material and catechol. Chromatography of the sulfonic acid esters (1.8 g) (solvent system A) gave three major components: 2-acetoxy-3-methoxybenzylsulfonic acid methyl ester (methyl ester of XXIII-acetate) (200 mg), recrystallized from ethyl acetate-petroleum ether (60–70 °C), m.p. 93–94 °C, 4-acetoxy-3-methoxybenzylsulfonic acid methyl ester (methyl ester of XXII-acetate) (700 mg), recrystallized from ethyl acetate-petroleum ether (60–70 °C),

m.p. 98–99 °C, 4-acetoxy-3-methoxy-1,5-bis(methoxysulfonylmethyl)-benzene (dimethyl ester of XXIV-acetate) (300 mg), recrystallized from ethyl acetate-petroleum ether (60–70 °C), m.p. 147.5–148.0 °C.

The three acetoxy-methoxybenzylsulfonic acid methyl esters were identical with the corresponding compounds obtained from I.

Two further components, were present in smaller amounts, but could not be isolated in pure form. Mass spectra indicated that they are methyl esters of diacetoxybenzylsulfonic acids, formed by sulfolytic demethylation of the appropriate methoxy compounds (XXII and XXIII), or by condensation of catechol with hydroxymethanesulfonic acid.

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