The Reactions of Lignin During Neutral Sulphite Pulping

Part IV.* The Behaviour of Structural Elements of the Pinoresinol Type

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The behaviour of structural elements of the pinoresinol type under the conditions of neutral sulphite pulping has been studied using (+)-pinoresinol and its dimethyl ether as model compounds.

The α-alkyl ether bond in the hydrofuran rings of pinoresinol is extensively cleaved giving rise to a mixture of α-, α, γ- and γ-sulphonic acids. The main components have been identified in the form of acetylated sulphonic acid methyl esters by analyses, NMR and mass spectra.

The dimethyl ether of pinoresinol remains essentially unaffected, only a small amount of sulphitolytic demethylation taking place. No condensation or polymerisation reactions have been observed after treatment of pinoresinol and its dimethyl ether with neutral sulphite under pulping conditions.

The results, interpreted in terms of the reaction routes outlined in Scheme 1, are consistent with the mechanism of sulphonation in *neutral* media previously proposed for structural elements of the β-aryl ether and phenylcoumaran types. They differ substantially from those obtained recently in the study of the sulphonation of pinoresinol in *acidic* media.

In the preceding communications of this series the behaviour of structural elements of the β-aryl ether [1,2] and phenylcoumaran [3] types towards neutral sulphite solutions under pulping conditions was described. It was found that the phenolic variants of these structures react extensively, yielding the corresponding α-sulphonic acids as intermediates [2,4] or as final products.[3,4] The non-phenolic structures of these types, however, turned out to be essentially stable under the conditions used.[1-4] On the basis of this marked difference in reactivity, the α-sulphonation of the phenolic β-aryl ethers and phenylcoumarans was interpreted as proceeding *via* the corresponding methylene quinone structures.[4]

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* Part III, see Ref. 2.

19

The present work deals with the reactions of pinoresinol (I) and its dimethyl ether (II) with neutral sulphite under pulping conditions. These compounds represent, respectively, phenolic and non-phenolic structures of the lignan type.

The behaviour of compounds I and II towards sulphite solutions at various pH-values has been investigated before.[5,6] Pinoresinol was treated with sulphite solutions of pH $6-9$ at 135° for 1.5 or 3 h and the sulphonation product isolated as the amorphous Ba-salt. By analogy with the product of sulphonation obtained from diveratryl ether, structure V was assigned to this product.[6] However, the analytical data did not agree with formula V.

Using the acetylation-methylation method described in our previous communications on the neutral [1-3] and acidic [7] sulphonation of lignin, it has now been possible to investigate the sulphonation of pinoresinol (I) with neutral sulphite solutions in more detail. The crude mixtures of acetylated sulphonic acid methyl esters obtained were separated by repeated preparative column chromatography and the main components were identified by analyses, NMR- and mass spectra. Since the preparative chromatographic separations were incomplete and involved substantial losses, the acetylated sulphonic acid methyl esters isolated in pure form account for a minor part only of their total amount present in the original reaction mixture. The esters decompose slowly as apparent from a continuous broadening of the melting point ranges on storage even at low temperatures. The deviations of the analyses from the calculated values are probably due to this instability and may indicate an elimination of methyl sulphurous acid taking place.

The most useful tool for the determination of the structures of the acetylated sulphonic acid methyl esters proved to be mass spectral fragmentation (see separate section; *cf.* also Ref. 7). NMR-spectrometry (see Table 1) provided data which support the structures given below.

RESULTS AND DISCUSSION

Pinoresinol (I) was treated with a neutral sulphite solution (initial pH 7.0, approximate pH during treatment 7.5,[8] final pH 10) at 180° for 3 h. From the reaction mixture were obtained: a disulphonic acid (VI),[4] a trisulphonic acid (VII) and two diastereoisomeric forms of a tetrasulphonic acid (VIII), isolated and identified as their acetylated sulphonic acid methyl esters (X, XI, and XII, respectively). Two further trisulphonic acids, presumably diastereoisomers of compound VII, as well as a second disulphonic acid containing one hydroxymethyl group (IX) were indicated (mass spectra, NMR-spectra). However, they could not be obtained as the pure acetylated sulphonic acid methyl esters (XI and XIII, respectively).

The conversion by neutral sulphite of pinoresinol into water-soluble sulphonic acids was almost quantitative (*cf.* also Ref. 6). The chloroform-ether extract from the aqueous reaction solution amounted to less than 1 % of the starting material and contained guaiacol and catechol only (thin-layer chromatography).

By contrast, pinoresinol dimethyl ether (II), when treated in the same way, reacted to a small extent only. The starting material was recovered in

Scheme 1.
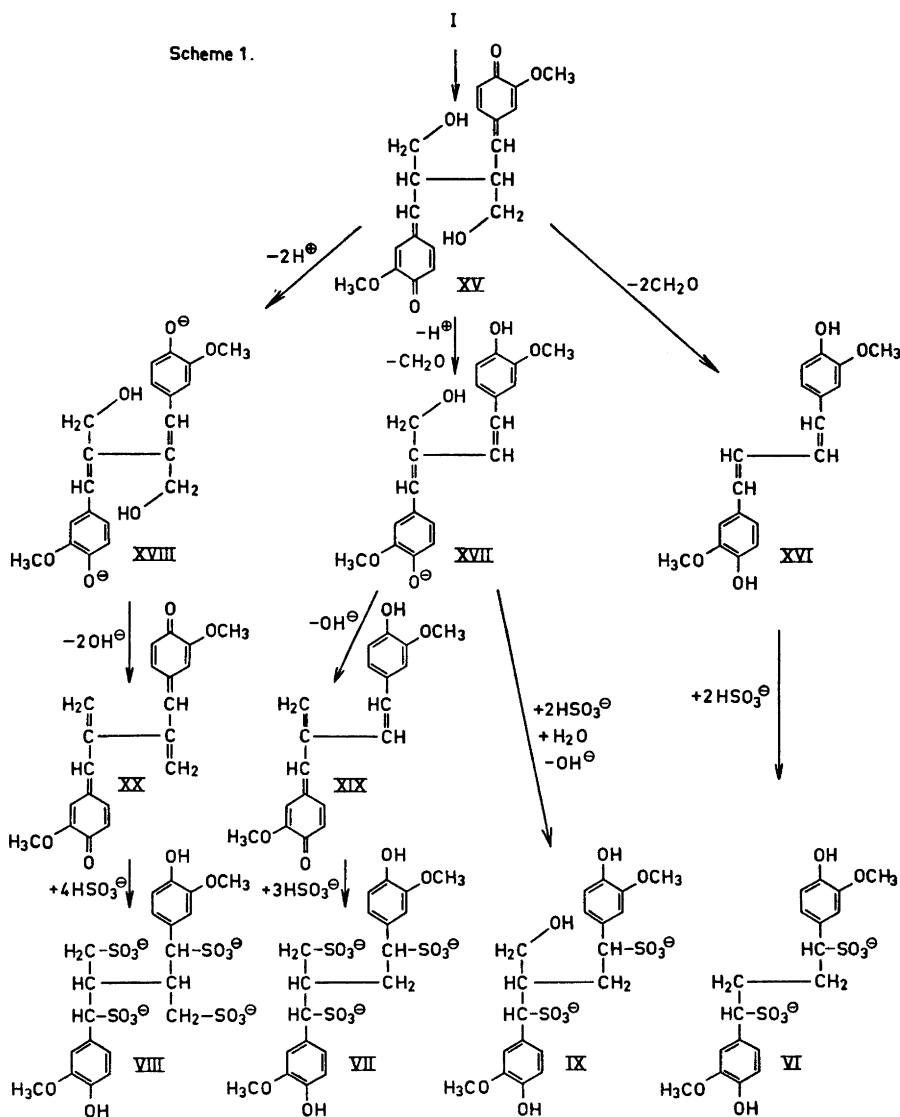
80 % yield from the chloroform-ether extract which also contained two demethylation products (III and IV). Paper chromatography of the aqueous solution revealed the presence of methanesulphonic acid (cf. also Refs. 1,3,4) and traces of other sulphonic acids which were not identified.

In Scheme 1 suggested routes for the formation of the sulphonic acids obtained from compound I are outlined. The extensive sulphonation of the
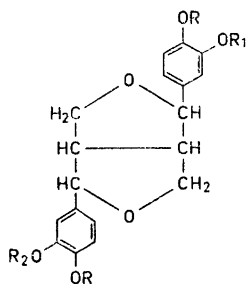
I   R = H, R_1 = R_2 = CH_3
II   R = R_1 = R_2 = CH_3
III   R = R_1 = CH_3, R_2 = $OCCH_3$
IV   R = CH_3, R_1 = R_2 = $OCCH_3$
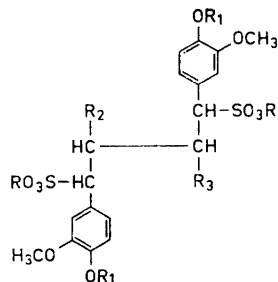
V   R = Ba/2, R_1 = H, R_2 = R_3 = CH_2OH
VI   R = R_1 = R_2 = R_3 = H
VII   R = R_1 = R_2 = H, R_3 = CH_2SO_3H
VIII   R = R_1 = H R_2 = R_3 = CH_2SO_3H
IX   R = R_1 = R_2 = H, R_3 = CH_2OH
X   R = CH_3, R_1 = $OCCH_3$, R_2 = R_3 = H
XI   R = CH_3, R_1 = $OCCH_3$, R_2 = H, R_3 = $CH_2SO_3CH_3$
XII   R = CH_3, R_1 = $OCCH_3$, R_2 = R_3 = $CH_2SO_3CH_3$
XIII   R = CH_3, R_1 = $OCCH_3$, R_2 = H, R_3 = CH_2OOCCH_3
XIV R_1 = H, R_2 = R_3 = CH_2OH. OH replacing SO_3R
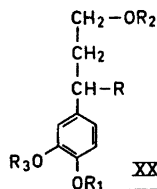
XXI   R = OH, R_1 = R_2 = H, R_3 = CH_3
XXII   R = SO_3H, R_1 = R_2 = H, R_3 = CH_3
XXIII   R = SO_3H, R_1 = R_2 = R_3 = H
XXIV   R = SO_3CH_3, R_1 = R_2 = $OCCH_3$, R_3 = CH_3
XXV   R = SO_3CH_3, R_1 = R_2 = R_3 = $OCCH_3$

phenolic compound (I) as opposed to the stability of its dimethyl ether (II) strongly suggests the intervention of a methylene quinone (XV)[4] in the reaction of I. This methylene quinone may eliminate β-protons and/or formaldehyde to yield the buta-1,3-diene structures XVI − XVIII. The hydroxymethyl-substituted buta-1,3-diene intermediates (XVII and XVIII) eliminate hydroxyl ions to give vinylogous methylene quinones (XIX and XX, respectively). The reaction sequences are terminated by the addition of bisulphite to the highly conjugated intermediates XVI, XVII, XIX, and XX affording the sulphonic acids VI, IX, VII, and VIII, respectively).

Experimental support for the first step (cleavage of the tetrahydrofuran rings with formation of the bis-methylene quinone XV) was provided by the finding that the tetra-ol XIV, on treatment with neutral sulphite, yielded the same mixture of sulphonic acids as that obtained from pinoresinol (paper chromatography). The reaction of compound XIV should proceed through the same methylene quinone (XV), as does the reaction of pinoresinol.

The subsequent steps, elimination of formaldehyde and/or of the elements of water, apparently require a $C_\beta - C_\beta$ linkage, as that present in lignan structures (*e.g.* in I), the generation of buta-1,3-diene intermediates providing the necessary driving force. Compound XXI which does not contain such a linkage gave the α-sulphonic acid XXII and its demethylation product XXIII only.

The reaction of bisulphite with the postulated vinylogous methylene quinone intermediates was demonstrated by treating coniferyl alcohol (XXVI) with a solution of neutral sulphite. This alcohol should form the vinylogous methylene quinone intermediate XXIX,[9] to which 1,8-addition of bisulphite should yield the coniferyl sulphonic acid XXVII, and 1,2-addition of bisulphite to

CH$_2$—R
|
HC
‖
CH

OCH$_3$
OR$_1$

XXVI R = OH, R$_1$ = H
XXVII R = SO$_3$H, R$_1$ = H
XXVIII R = SO$_3$CH$_3$, R$_1$ = OCCH$_3$

CH$_2$
‖
HC
|
CH

OCH$_3$
O

XXIX

CH$_2$—SO$_3$R
|
CH$_2$
|
CH—SO$_3$R

OCH$_3$
OR$_1$

XXX R = R$_1$ = H
XXXI R = CH$_3$, R$_1$ = OCCH$_3$

CH$_2$OH   CH$_2$
| ‖
HC ———— C
| |
HC   CH

OCH$_3$ OCH$_3$
OH   O

XXXII

CH$_2$OR$_1$ CH$_2$—SO$_3$R
| |
HC ———— C
| ‖
HC   CH

OCH$_3$ OCH$_3$
OR$_1$ OR$_1$

XXXIII R = R$_1$ = H
XXXIV R = CH$_3$, R$_1$ = OCCH$_3$

CH$_2$OR$_1$ CH$_2$—SO$_3$R
| |
HC ———— CH
| |
HC   CH—SO$_3$R

OCH$_3$ OCH$_3$
OR$_1$ OR$_1$

XXXV R = R$_1$ = H
XXXVI R = CH$_3$, R$_1$ = OCCH$_3$
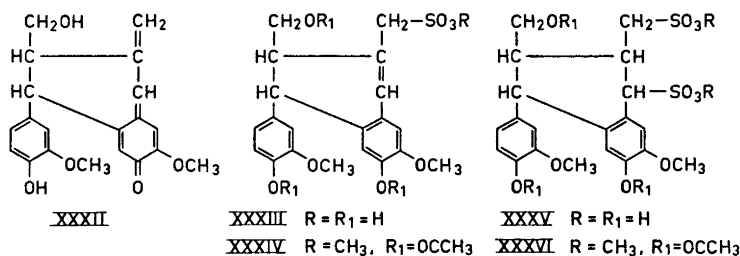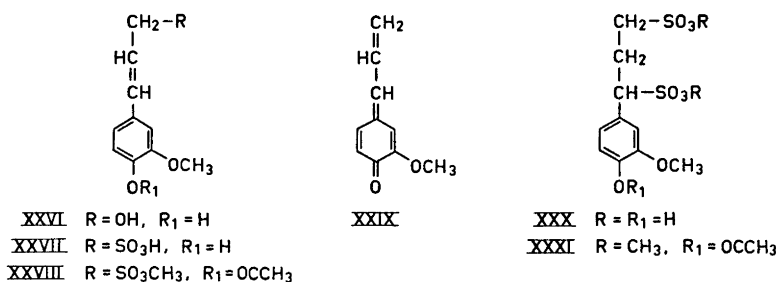
XXVII, finally, should give rise to the α,γ-disulphonic acid XXX. In fact, disulphonic acid XXX was obtained in a high yield (cf. also neutral sulphonation of sinapyl alcohol[10]). To confirm these successive additions of bisulphite, the sulphonation was carried out in two steps starting from a vinylogous [methylene quinone (XXXII) derived from a cyclolignan ring system.

The methylene quinone XXXII was obtained by treating pinoresinol with hydrogen bromide in chloroform and extracting the chloroform solution with a solution of bicarbonate.[9] Apparently, condensation between an α-position and the 6-position in the non-adjacent ring takes place under the conditions of the treatment with hydrogen bromide (cf. also Refs. 11 and 7). The cross-conjugated, vinylogous bis-methylene quinone XX, previously [9] suggested to be formed during the above treatment, was not observed.

Reaction of the methylene quinone XXXII with sulphite at room temperature yielded the cyclolignen-γ-sulphonic acid XXXIII (1. step). Heating an aqueous solution of the latter with neutral sulphite at 180° afforded the expected α,γ-disulphonic acid XXXV (2. step), which on storage at room temperature slowly eliminated bisulphite regenerating the cyclolignen-γ-sulphonic acid (XXXIII).

When the pH of the sulphite solution was kept constant at 7.0 throughout the treatment by using a greater excess of sulphite, compound I gave the above cyclolignen-γ-sulphonic acid XXXIII together with the sulphonic acids VI – IX, depicted in Scheme 1. Presumably the formation of XXXIII follows a route analogous to that of the generation of cyclolignan-α-sulphonic acids which takes place in more acidic media.[7] This route should include the following steps: epimerisation of pinoresinol, opening of the tetrahydrofuran ring not involved in the epimerisation step, electrophilic attack of the benzylic carbon on the 6-position of the non-adjacent ring and cleavage of the second tetrahydrofuran ring to yield a methylene quinone derived from the corresponding cyclolignan. Elimination of the elements of water from the latter then affords the vinylogous methylene quinone XXXII which finally adds bisulphite to give the sulphonic acid XXXIII (*cf.* also the addition of bisulphite to the vinylogous methylene quinone XXIX described above). Addition of further bisulphite to the cyclolignen sulphonic acid XXXIII may have yielded cyclolignan disulphonic acid XXXV, although this acid, due to its instability, could not be isolated from the reaction mixture.

The formation of the methylene quinone intermediate XV, the elimination of formaldehyde, and the addition of bisulphite are steps analogous to those observed in the reactions of structural elements of the β-aryl ether,[1,2] phenylcoumaran,[3] and presumably also 1,2-diaryl-propane-1,3-diol types during neutral sulphite pulping.[4] These steps also bear strong resemblance to the reactions of the same compound (I) during alkali- and sulphate pulping.[4] The elimination of formaldehyde (step XV→XVI) under the latter conditions has recently [12] been demonstrated by the isolation (as diacetates) of 1,4-bis-(4-hydroxy-3-methoxy-phenyl)-buta-1,3-diene (XVI) and of bis-(4-hydroxy-3-methoxy-phenyl)-methane, a secondary condensation product of formaldehyde with the guaiacol liberated during the pulping treatments.

On the other hand, the mechanism of sulphonation of pinoresinol during neutral sulphite pulping differs substantially from that operating in *acidic* media.[4] Under the latter conditions the reactions proceed through benzylium ions and pinoresinol is converted into two diastereoisomeric cyclolignan-α-sulphonic acids.[4,7] The conditions of neutral sulphite pulping (pH ≥ 7) and of acidic sulphite pulping (pH ~ 1.5) represent extremes yielding different types of sulphonic acids (*cf.* also sulphonations of β-aryl ethers [1,2,4,7] and of phenylcoumarans [3,4,7]). At medium pH values, mixtures of these two types of sulphonic acids may be expected. The cyclolignen-γ-sulphonic acid XXXIII, observed in the present study only when the initial pH of the sulphite solution (7.0) was kept constant, seems to be formed preferentially in this medium pH range.

Thus, structural elements of the pinoresinol type, although possibly present in minor amounts only,[13] contribute to the sulphonation of lignin in neutral media. The sulphonic acid groups become attached to the α- and/or γ-carbon atom(s). Most of the reaction steps involved are analogous to those observed with other types of phenolic structures under the conditions of neutral sulphite pulping. The above results also suggest reactions of certain extractives of the lignan type (*e.g.* pinoresinol, syringaresinol, lariciresinol, olivil) during this process.

EXPERIMENTAL

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

Paper chromatography. The aqueous solutions containing acetylated sulphonic acids were investigated by paper chromatography using Whatman No. 3 paper and a mixture of butanol-acetic acid-pyridine-water (15:3:10:12) as solvent. Bromophenol blue served as spray reagent.

Thin-layer and column chromatography. Sulphonic acid esters were investigated on the analytical scale by TLC using silica gel HF_{254} (E. Merck A. G., Darmstadt). The preparative separations were carried out by column chromatography using silicic acid (SilicAR CC-7 100−200 mesh, Mallinckrodt). The solvent systems used are described below.

NMR-spectrometry. The NMR-spectra were run on a Perkin-Elmer R-12 spectrometer. $CDCl_3$ was used as solvent unless otherwise stated. The NMR-data are summarised in Table 1. Chemical shifts (δ-values) are given in ppm downfield from tetramethylsilane.

Mass-spectrometry. The 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 $130-180°$. The mass spectral fragmentations are outlined in a separate section (see below).

Model compounds. The compounds used in this study were prepared as previously described (see Refs. 14−16).

Sulphite solution. $Na_2S_2O_5$ (0.25 mol) in distilled water (1 l) was adjusted to pH 7 with 2 N NaOH.

Conditions of the sulphite treatment. The model compound suspended in the sulphite solution was heated in a stainless steel autoclave at 180° for 3 h.

Working-up procedure. The working-up procedure was the same as that previously described.[7]

Treatment of pinoresinol (I)

Pinoresinol (4.0 g) was treated with the sulphite solution (160 ml) (pH after the treatment ≈10). The chloroform−ether extract (<1 %) contained guaiacol and catechol (TLC in chloroform−acetone 9:1). In the aqueous solution four sulphonic acids and traces of methanesulphonic acid were found (paper chromatography).
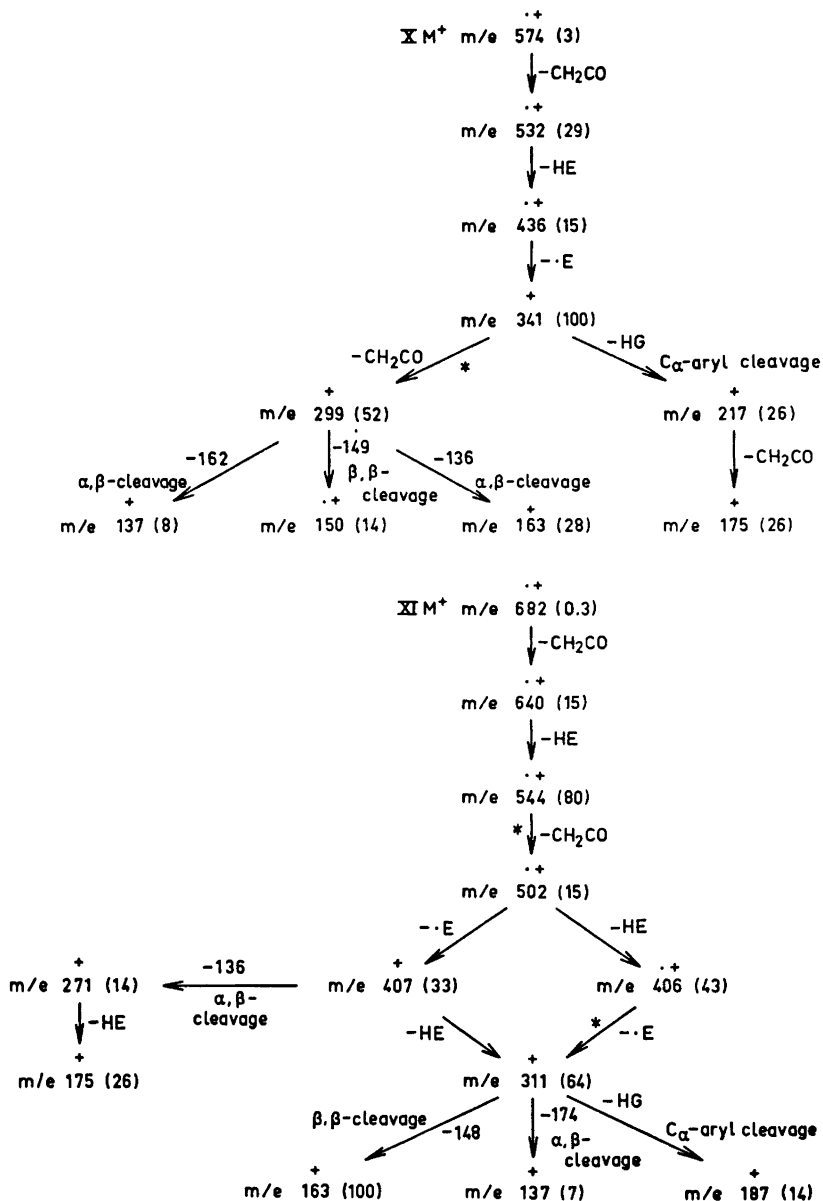
TLC after acetylation and methylation using benzene−acetone (4:1) revealed a more complex composition showing at least six spots. By preparative column chromatography using the same solvent system four main fractions were obtained: fraction 1 (fastest moving) (1.3 g), fraction 2 (2.5 g), fraction 3 (0.25 g), fraction 4 (1.0 g). From these four fractions, amounting totally to more than 5 g, the four main components given below were obtained in pure form as acetylated methyl esters in a total yield of 1.57 g only. The considerable losses were due to incomplete separations of the components by the chromatographic method used.

Fraction 1. TLC using benzene-acetone (9:1) as solvent system (run five times) showed the presence of three components (one in trace amount). Preparative column chromatography using the same solvent did not effect a complete separation of these but the slowest moving component was obtained in pure form by repeated recrystallisations from ethyl acetate-petroleum ether (40−60°).

1,4-Bis-(3-methoxy-4-acetoxy-phenyl)-butane-1,4-disulphonic acid dimethyl ester (X) was obtained in 100 mg yield. M.p. $128-131°$. (Found: C 49.98; H 5.37; O 33.58; S 11.07. $C_{24}H_{30}O_{12}S_2$ requires: C 50.17; H 5.26; O 33.41; S 11.16). The other main component from fraction 1 could not be obtained in pure form. Mass spectral data clearly indicated that the substance is a diastereoisomer of the acetylated trisulphonic acid trimethyl ester (XI) obtained from fraction 2 (see below).

Fraction 2. TLC using benzene-ethyl acetate (3:2) (run three times) showed the presence of three components (one in minor amount). One of the major components could be separated by fractional crystallisation from ethyl acetate-petroleum ether (40−60°). The compound was recrystallised from ethyl acetate.

1,4-Bis- (3 -methoxy- 4 -acetoxy-phenyl) - 2 - (methoxysulphonyl-methyl) -butane-1,4-disulphonic acid dimethyl ester (XI) was obtained in 900 mg yield. After two recrystallisations from ethyl acetate the compound melted at $166-167°$. (Found: C 46.33; H 5.19; O 34.38; S 13.84. $C_{26}H_{34}O_{15}S_3$ requires: C 45.74; H 5.02; O 35.15; S 14.09). The other two com-

$\textbf{X}\,M^+$ m/e 574 (3)

↓ -CH₂CO

m/e 532 (29)

↓ -HE

m/e 436 (15)

↓ -·E

m/e 341 (100)

-CH₂CO ↙ *   ↘ -HG   Cα-aryl cleavage

m/e 299 (52)   m/e 217 (26)

-162 ↙   ↓-149   ↘ -136   ↓ -CH₂CO

α,β-cleavage   β,β-   α,β-cleavage

m/e 137 (8)   m/e 150 (14)   m/e 163 (28)   m/e 175 (26)

$\textbf{XI}\,M^+$ m/e 682 (0.3)

↓ -CH₂CO

m/e 640 (15)

↓ -HE

m/e 544 (80)

*↓ -CH₂CO

m/e 502 (15)

-·E ↙   ↘ -HE

m/e 407 (33)   m/e 406 (43)

-136 ← α,β-cleavage

m/e 271 (14)

↓ -HE

m/e 175 (26)

-HE ↘   ↗* -·E

m/e 311 (64)

β,β-cleavage ↙ -148   ↓ -174   ↘ -HG   Cα-aryl cleavage
                        α,β-cleavage

m/e 163 (100)   m/e 137 (7)   m/e 187 (14)

ponents in fraction 2 (approximately 50 %) could not be completely separated by chromatography. The mass spectral fragmentation given by the predominating component of the mixture was identical to that given by the pure acetylated trisulphonic acid trimethyl ester (XI) and indicates a further diastereoisomer of this compound. The additional peaks of the mass spectrum, attributable to the minor component, could not

Table 1. Proton chemical shifts (δ-values in ppm) of acetylated sulphonic acid methyl esters.

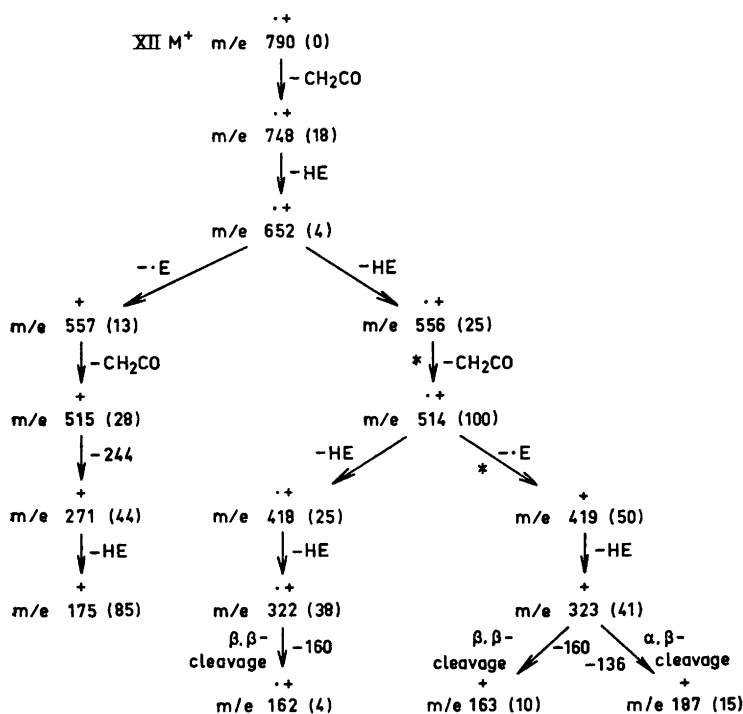| Compound	Aromatic H	Aliphatic H	OCH$_3$ (ether and ester)	OCCH$_3$ aromatic	OCCH$_3$ aliphatic
X[a]	centred at 7.0 (6H)	centred at 4.40 (2H$_\alpha$)(t) centred at 2.20 (4H$_\beta$)(m)	3.73 (6H)(s)	2.22 (6H)(s)	
XI[a]	centred at 7.0 (6H)	centred at 4.45 (4H) centred at 2.25 (3H)	3.82 (3H)(s) 3.80 (6H)(s) 3.70 (6H)(s)	2.28 (3H)(s) 2.24 (3H)(s)	
XII a[a]	centred at 7.0 (6H)	centred at 4.42 (6H) centred at 2.25 (2H)	3.81 (6H)(s) 3.79 (3H)(s) 3.78 (3H)(s) 3.70 (6H)(s)	2.28 (6H)(s)	
XII b[a]	centred at 7.1 (6H)	centred at 4.45 (6H) centred at 2.30 (2H)	3.81 (6H)(s) 3.76 (6H)(s) 3.70 (6H)(s)	2.28 (6H)(s)	
XXIV	7.00 (3H)	centred at 4.2 (3H) centred at 2.6 (2H)	3.84 (3H)(s) 3.67 (3H)(s)	2.29 (6H)(s)	1.98 (3H)(s)
XXV	7.25 (3H)	centred at 4.2 (3H) centred at 2.6 (2H)	3.63 (3H)(s)	2.25 (6H)(s)	1.93 (3H)(s)
XXXI	7.02 (3H)	centred at 4.5 (1H) centred at 3.1 (2H) centred at 2.8 (2H)	3.84 (6H)(s) 3.71 (3H)(s)	2.29 (3H)(s)	
XXXIV	centred at 6.7 (5H)	6.7 (1H$_{C_4}$) centred at 4.1 (2H) 3.89 (2H)(s) 3.5 – 4.0 (1H$_{C_1}$) 3.05 (1H$_{C_2}$)	3.80 (3H)(s) 3.67 (3H)(s) 3.37 (3H)(s)	2.21 (6H)(s)	1.98 (3H)(s)
Dibromo-compound of XXXIV	centred at 6.8 (4H) 6.24 (1H)(s)	4.56 (1H$_{C_4}$)(d) centred at 4.1 (2H) centred at 3.91 (2H) 3.5 – 4.0 (1H$_{C_1}$) 2.96 (1H$_{C_2}$)(m)	3.85 (3H)(s) 3.51 (3H)(s) 3.44 (3H)(s)	2.24 (3H)(s) 2.21 (3H)(s)	2.01 (3H)(s)

Table 1. Continued.

| XXXVI | centred at 6.7 (5H) | centred at 4.2 (3H) centred at 3.9 (2H) $3.5 - 4.0$ ($1H_{C_1}$) centred at 3.1 ($1H_{C_2}$) $1H_{C_3}^{\ b}$ | 3.86 (3H)(s) 3.68 (3H)(s) 3.39 (3H)(s) 2.96 (3H)(s) | 2.23 (3H)(s) 2.22 (3H)(s) | 2.00 (3H)(s) |

^{a} Solvent: acetonitrile-d_3.
^{b} Location uncertain.

be completely rationalised. The elimination of two ketene-, two methyl sulphurous acid (HE)-, and one acetic acid (HA) fragment were clearly discernible, suggesting an acetylated disulphonic acid dimethyl ester containing an acetoxy group linked to a side chain (XIII). The NMR-spectrum was compatible with structure XIII. Signals exhibited by the protons of four methoxyl groups and by those of three acetoxy groups (one linked to an aliphatic carbon atom) were observed.

Fraction 3. TLC using benzene − ethyl acetate (13:7) (run three times) showed the presence of three components. The two minor ones appeared to be contaminations from fractions 2 and 4. The third and main component could not be obtained sufficiently pure for analysis.

XII M$^+$ m/e 790 (0)
   $\downarrow$ $-CH_2CO$
m/e 748 (18)
   $\downarrow$ $-HE$
m/e 652 (4)
   $-\cdot E$ ⟋   ⟍ $-HE$
m/e 557 (13)   m/e 556 (25)
   $\downarrow$ $-CH_2CO$ * $\downarrow$ $-CH_2CO$
m/e 515 (28)   m/e 514 (100)
   $\downarrow$ -244 $-HE$ ⟋   ⟍ $-\cdot E$ *
m/e 271 (44)   m/e 418 (25)   m/e 419 (50)
   $\downarrow$ $-HE$ $\downarrow$ $-HE$ $\downarrow$ $-HE$
m/e 175 (85)   m/e 322 (38)   m/e 323 (41)
     β,β- $\downarrow$ -160 β,β- ⟋ -160 -136 ⟍ α,β-
   cleavage   cleavage   cleavage
     m/e 162 (4)   m/e 163 (10)   m/e 187 (15)

Fraction 4. The presence of two components was shown by TLC using benzene – ethyl acetate (3:2) (run three times). They were separated on a preparative scale by column chromatography using the same solvent system.

1,4-Bis-(3-methoxy-4-acetoxy-phenyl)-2,3-bis-(methoxysulphonyl-methyl)-butane-1,4-di-sulphonic acid dimethyl ester (XII) (first form) (200 mg) was obtained after recrystallisation from ethyl acetate-petroleum ether (40 – 60°); m.p. 196 – 198°. (Found: C 43.82; H 5.03; O 35.24; S 15.45. $C_{28}H_{38}O_{18}S_4$ requires: C 42.52; H 4.84; O 36.41; S 16.23).

1,4-Bis-(3-methoxy-4-acetoxy-phenyl)-2,3-bis-(methoxysulphonyl-methyl)-butane-1,4-di-sulphonic acid dimethyl ester (XII) (second form) (370 g) was obtained after recrystallisation from ethyl acetate-petroleum ether (40 – 60°); m.p. 185 – 187°. (Found: C 43.90; H 5.15; O 35.02; S 15.44. $C_{28}H_{38}O_{18}S_4$ requires: C 42.52; H 4.84; O 36.41; S 16.23).

If the excess of sulphite was increased to 80 ml sulphite solution per 1 g of pinoresinol, the pH of the sulphite solution was kept between 7 – 8 during the treatment. Under these conditions an additional fraction containing a further sulphonic acid was obtained. On paper chromatography this sulphonic acid showed the same R_F-value as did the two diastereoisomeric forms of the cyclolignan sulphonic acid formed during treatment of pinoresinol with acidic sulphite solutions.[7] TLC of the mixture of acetylated sulphonic acid methyl esters also showed the presence of one additional spot. A small amount of this compound was obtained in pure form by preparative chromatography using benzene – ethyl acetate (7:3). The NMR spectrum showed that the compound had structure XXXIV and was identical to that obtained by treatment of the methylene quinone (XXXII) from pinoresinol with a neutral sulphite solution at room temperature (see below).

Treatment of pinoresinol dimethyl ether (II)

Pinoresinol dimethyl ether (2.0 g) was treated with the sulphite solution (80 ml) (pH after the treatment = 7). The chloroform-ether extract (1.8 g) contained starting material and small amounts of two other components (TLC using chloroform). These were separated by column chromatography using the same solvent. Pinoresinol dimethyl ether (1.6 g) was recovered: yield (80 %). The other two components turned out to be demethylation products of pinoresinol dimethyl ether. These were converted into their acetates and analysed.

Demethylation products. Compound III (150 mg) was obtained as colourless crystals; m.p. 83.0 – 85.5°. (Found: C 66.75; H 6.48; O 26.89. $C_{23}H_{26}O_7$ requires: C 66.66; H 6.32; O 27.02). Compound IV (20 mg) was obtained as a colourless liquid. (Found: C 65.56; H 5.42; O 28.39. $C_{24}H_{26}O_8$ requires: C 65.15; H 5.92; O 28.93).

The NMR spectra of the acetylated demethylation products III and IV (solvent: CDCl₃) showed the expected singlets due to the protons of the methoxyl- and acetyl groups at $\delta = 3.89 - 3.80$ ppm and 2.31 – 2.28 ppm, respectively. The signals for the aliphatic protons were similar to those reported for compound I (see Ref. 17).

The aqueous solution contained methanesulphonic acid and traces of other sulphonic acids (paper chromatography). These were not further investigated.

Treatment of 1,4-bis-(4-hydroxy-3-methoxy-phenyl)-2,3-bis-(hydroxymethyl)-butane-1,4-diol (XIV)

Compound XIV (850 mg) was treated with the sulphite solution (80 ml) (pH after the treatment = 7). The chloroform-ether extract contained traces of guaiacol and catechol (< 1 %). The aqueous solution contained the same sulphonic acids as those obtained by neutral sulphite treatment of pinoresinol (I) (paper chromatography, TLC after acetylation and methylation). The mixture of acetylated sulphonic acid methyl esters was not separated.

Treatment of 1-(4-hydroxy-3-methoxy-phenyl)-1,3-dihydroxy-propane (XXI)

Compound XXI (1.0 g) was treated with the sulphite solution (80 ml) (pH after the treatment = 7). The chloroform-ether extract contained traces of the starting material (TLC using benzene — acetone 19:1). The aqueous solution contained methanesulphonic acid and two further components (paper chromatography). TLC of the acetylated methyl esters using benzene — acetone (19:1) also showed three components. These were separated on a preparative scale using the same solvent system. Methanesulphonic acid methyl ester was not further characterised.

1-(4-Acetoxy-3-methoxy-phenyl)-3-acetoxy-propane-1-sulphonic acid methyl ester (XXIV) was obtained in 74 % yield as a colourless liquid. (Found: C 49.87; H 5.41; O 35.52; S 8.78. $C_{15}H_{20}O_8S$ requires: C 49.99; H 5.59; O 35.52; S 8.90).

Treatment of compound XXI with *acidic* sulphite afforded the same product (XXIV) in 90 % yield. The chloroform-ether extract contained starting material only.

1-(3,4-Diacetoxy-phenyl)-3-acetoxy-propane-1-sulphonic acid methyl ester (XXV) was obtained as a colourless liquid in 9 % yield. (Found: C 49.27; H 5.11; O 36.87; S 8.75. $C_{16}H_{20}O_9S$ requires: C 49.48; H 5.19; O 37.07; S 8.26).

Treatment of coniferylalcohol diacetate

Coniferylalcohol (XXVI) diacetate (550 mg) was treated with the sulphite solution (18 ml). The chloroform-ether extract contained traces of polymeric material (< 1 %). The aqueous solution contained one sulphonic acid.

1-(4-Acetoxy-3-methoxy-phenyl)-propane-1,3-disulphonic acid dimethyl ester (XXXI), colourless liquid, yield 90 %. (Found: C 42.26; H 4.94; O 36.17; S 16.26. $C_{14}H_{20}O_9S_2$ requires: C 42.42; H 5.08; O 36.32; S 16.18). The mass spectrum contained the peaks 396 (3 %), 354 (16 %), 259 (67 %), 163 (100 %), 131 (84 %) and can be rationalised in terms of the successive losses of ketene, of the methyl sulphurous acid radical, $\cdot SO_2OCH_3$, of methyl sulphurous acid, HSO_2OCH_3, and of methanol.
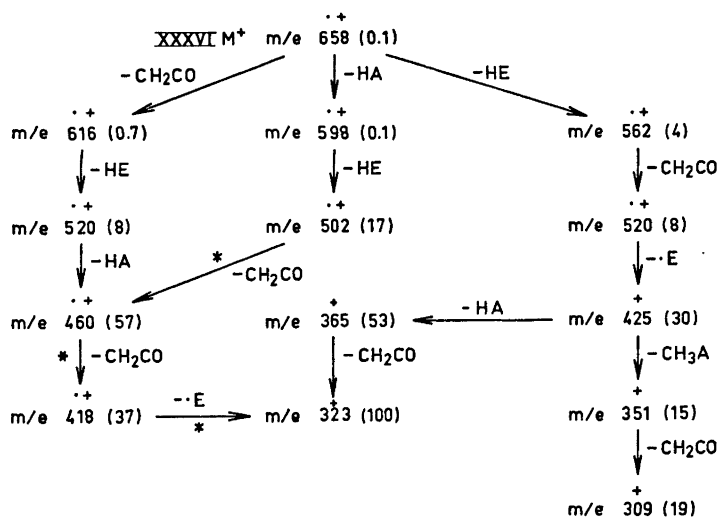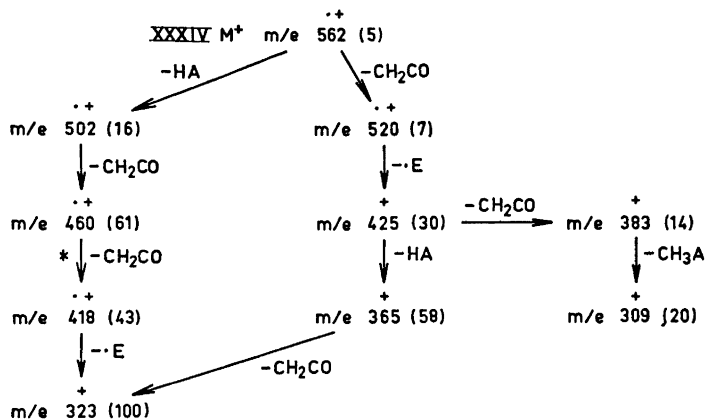
Preparation and neutral sulphite treatment of the methylene quinone (XXXII) from pinoresinol

Chloroform (free from ethanol, 1 l) was saturated with dry HBr. To this solution pinoresinol (2.0 g) dissolved in chloroform (15 ml) was added. After 3 min the solution was neutralised by shaking with a saturated aqueous solution of sodium bicarbonate. The chloroform solution (containing the methylene quinone) was filtered and treated with the neutral sulphite solution (80 ml) by vigorous shaking at room temperature for 60 min. The aqueous layer was separated and worked up as previously described.[7] Acetylated sulphonic acid methylester (900 mg) was obtained. TLC using benzene-ethyl acetate (3:2) showed the presence of only one component together with a small amount of polymeric material. A preparative separation by column chromatography was carried out using the same solvent.

7-Acetoxy-6-methoxy-2-acetoxymethyl-1-(4'-acetoxy-3'-methoxy-phenyl)-1,2-dihydronaphthalene-3-methylsulphonic acid methyl ester. (4,4',9-triacetoxy-3,3'-dimethoxy-cyclolign-7'-en-9'-sulphonic acid methyl ester.*) (XXXIV) (650 mg) was obtained as colourless liquid. (Found: C 57.47; H 5.40; O 31.37; S 5.84. $C_{27}H_{30}O_{11}S$ requires: C 57.64; H 5.38; O 31.28; S 5.70). For further characterisation of the cyclolignen sulphonic acid (XXXIII) the acetylated methyl ester (XXXIV) (200 mg) dissolved in chloroform (10 ml) was reacted with bromine at room temperature for 30 min. The resulting dibromo compound was purified by preparative column chromatography using benzene-ethyl acetate (3:2) as the solvent system.

7-Acetoxy-6-methoxy-2-acetoxymethyl-3,4-dibromo- (4'-acetoxy-3'-methoxy-phenyl)-1,2,3,4-tetrahydronaphthalene-3-methylsulphonic acid methyl ester was obtained in 190 mg yield.

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* Nomenclature according to Ref. 18.

XXXIV M+ m/e 562 (5)

-HA → m/e 502 (16)
-CH2CO → m/e 520 (7)

m/e 502 (16) ─ -CH2CO → m/e 460 (61)
m/e 460 (61) ─ * -CH2CO → m/e 418 (43)
m/e 418 (43) ─ -·E → m/e 323 (100)

m/e 520 (7) ─ -·E → m/e 425 (30)
m/e 425 (30) ─ -CH2CO → m/e 383 (14)
m/e 425 (30) ─ -HA → m/e 365 (58)
m/e 383 (14) ─ -CH3A → m/e 309 (20)
m/e 365 (58) ─ -CH2CO → m/e 323 (100)

XXXVI M+ m/e 658 (0.1)

-CH2CO → m/e 616 (0.7)
-HA → m/e 598 (0.1)
-HE → m/e 562 (4)

m/e 616 (0.7) ─ -HE → m/e 520 (8)
m/e 520 (8) ─ -HA → m/e 460 (57)
m/e 460 (57) ─ * -CH2CO → m/e 418 (37)
m/e 418 (37) ─ -·E * → m/e 323 (100)

m/e 598 (0.1) ─ -HE → m/e 502 (17)
m/e 502 (17) ─ * -CH2CO → m/e 365 (53)
m/e 365 (53) ─ -CH2CO → m/e 323 (100)

m/e 562 (4) ─ -CH2CO → m/e 520 (8)
m/e 520 (8) ─ -·E → m/e 425 (30)
m/e 425 (30) ─ -HA → m/e 365 (53)
m/e 425 (30) ─ -CH3A → m/e 351 (15)
m/e 351 (15) ─ -CH2CO → m/e 309 (19)

The compound eliminates one molecule of hydrogen bromide on storage. (Found: C 50.34; H 4.64; O 27.30; Br 12.64; S 4.90. $C_{27}H_{30}O_{11}Br_2S - HBr$ requires: C 50.54; H 4.56; O 27.44; Br 12.46; S 5.00).

Treatment of the cyclolignen sulphonic acid (XXXIII) with neutral sulphite solution at 180°

Pinoresinol (1.5 g) was reacted with HBr in saturated chloroform solution (500 ml) during 8 min. After neutralisation with aqueous sodium bicarbonate the resulting solution of the methylene quinone (XXXII) was reacted with a solution of neutral sulphite at room temperature for 1 h. The aqueous layer was then immediately heated to 180° and kept at this temperature for 3 h. Following the usual working-up procedure, a crude acetylated sulphonic acid methyl ester (400 mg) was obtained. (The chloroform-ether

extract yielded 30 mg of guaiacol and catechol identified by TLC in chloroform-acetone 9:1). Thin-layer chromatography using benzene-ethyl acetate (3:2) as the solvent system showed the presence of one major component and of a small amount of polymeric material. Preparative column chromatography using the same solvent yielded the pure compound as a colourless liquid (300 mg).

7-Acetoxy-6-methoxy-2-acetoxymethyl-3-methylsulphonic acid methyl ester-1-(4'-acetoxy-3'-methoxy-phenyl)-1,2,3,4-tetrahydronaphthalene-4-sulphonic acid methyl ester (4,4',9-tri-acetoxy-3,3'-dimethoxy-cyclolignan-7',9'-disulphonic acid dimethyl ester*) (XXXIV). (Found: C 51.17; H 5.34; O 33.86; S 9.78. $C_{28}H_{34}O_{14}S_2$ requires: C 51.06; H 5.20; O 34.00; S 9.74).

Mass spectral fragmentations

Mass spectrometry was used for the determination of the structures of the acetylated sulphonic acid methyl esters X – XII, XXXI, XXXIV, and XXXVI (*cf.* also Ref. 7). The fragmentation paths outlined below showed the following common patterns:

(1) Elimination of ketene, of methyl sulphurous acid, HSO_2OCH_3 (HE) and of the methyl sulphurous ester radical, $\cdot SO_2OCH_3$ ($\cdot$E).

(2) Cleavage of the $C_\alpha - C_\beta$, $C_\beta - C_\beta$ and C_α-aryl linkages (in compounds X – XII).

All fragments exceeding 3 % rel. abundance are accounted for. Only clearly distinguishable metastable ions are given. They are designated by an asterisk (*).

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