

## The Reactions of Lignin during Sulphate Cooking

### Part X.\* Synthesis and Alkaline Treatment of Model Compounds Representing Intermediary Episulphide Structures\*\*

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Three (4-acetoxy-3-methoxy-phenyl)-substituted episulphides (VII-IX) were prepared by epoxidation of the corresponding olefins (I-III) with perbenzoic acid and treatment of the epoxides (IV-VI) with thiourea.

When treated with 2 N sodium hydroxide at room temperature or at 100°, the episulphides (VII-IX) afforded the corresponding *p*-dithianes (X-XII). The latter were found to be identical with the dithianes previously<sup>1</sup> obtained by alkaline treatment of the corresponding  $\beta$ -mercaptoalkyl-arylethers. This result further supports the suggested course of splitting of  $\beta$ -mercaptoalkyl-arylethers *via* episulphides.

The dithianes (X and XI) were also prepared by treating the corresponding dibromo compounds (XIII and XIV, respectively) with sodium sulphide.

Some configurational relationships were elucidated by PMR-measurements.

Recently the mechanism of splitting of  $\beta$ -arylether bonds in phenolic lignin units during sulphate cooking has been elucidated (for a mechanistic scheme see Part VIII, Ref. 1). Model compounds representing intermediary structures were prepared and treated with white liquor\*\*\* or 2 N sodium hydroxide under the appropriate conditions. All the intermediates investigated gave the corresponding *p*-dithianes as final products. This result was in agreement with the proposed course of splitting<sup>1,2</sup> involving intermediary episulphide structures.

\* Part IX. Gierer, J. and Wallin, N. H. *Acta Chem. Scand.* **19** (1965) 1502.

\*\* A preliminary report of the results of this work was given at the "12. Nordiske Kjemikermøte", Trondheim, June 16-20, 1965.

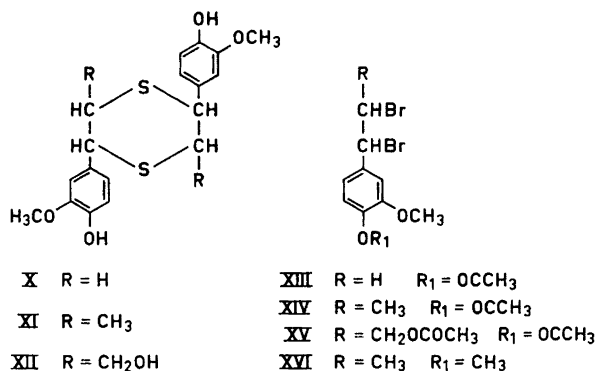
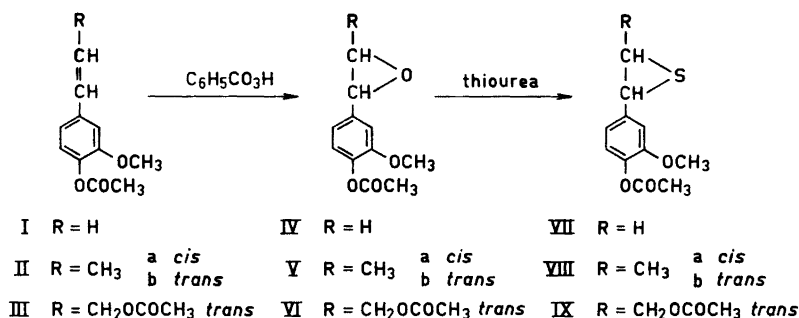
\*\*\* The term "white liquor" refers to a solution of NaOH (3.5 g) and Na<sub>2</sub>S·9 H<sub>2</sub>O (3.1 g) in water (100 ml).

To further support this mechanism it seemed desirable to synthesise model compounds of the episulphide type and to examine the ability with which they could be converted into *p*-dithianes by the action of 2 N sodium hydroxide.

## RESULTS AND DISCUSSION

The episulphides (VII–IX) were prepared by epoxidation of the corresponding ( $\omega$ -substituted) 4-acetoxy-3-methoxy-styrenes (I–III) with perbenzoic acid in chloroform followed by reaction of the epoxides (IV–VI) with thiourea in methanol.

Epoxidation of olefins by the action of peroxy acids is known to proceed by *cis*-addition.<sup>3</sup> Replacement of oxygen for sulphur, involving *trans*-opening



of the epoxide ring and *trans*-closing of the episulphide ring, proceeds with two Walden inversions.<sup>4</sup> Thus, starting from *trans*-isoeugenolacetate (IIb) and from *trans*-coniferylalcohol-diacetate (III), the formation of the *trans*-epoxy (Vb and VI) and *trans*-epithio (VIIIb and IX) compounds could be predicted. Conversely, the *cis*-form of isoeugenolacetate (IIa) could be expected to give the corresponding *cis*-epoxy (Va) and *cis*-epithio (VIIIa) compounds. These configurational relationships were confirmed by means of proton magnetic resonance spectroscopy.

The values of the chemical shifts (in ppm) and of the spin coupling constants (in cps) for the compounds prepared are given in Table 1. As can be seen, the *trans*-olefinic protons (*e.g.* in compound IIb) having a dihedral angle of  $180^\circ$  show a larger vicinal coupling constant ( $J_{\alpha\beta} = 16$  cps) than the *cis*-olefinic protons (dihedral angle  $= 0^\circ$ ,  $J_{\alpha\beta} = 11.5$  cps). About the same values (17.2 cps and 11.0 cps) were obtained for the vicinal couplings of the vinylic protons in compound I. The coupling constants found agree reasonably well with those calculated from the equations derived by Williamson and Johnson<sup>5</sup> ( $J_{\alpha\beta} = 10 \times \cos^2 \varphi$ , for  $0^\circ \leq \varphi \leq 90^\circ$ , and  $J = 16 \times \cos^2 \varphi$ , for  $90^\circ \leq \varphi \leq 180^\circ$ , where  $\varphi$  is the H—C—C—H dihedral angle). Coniferylalcohol diacetate (III) exhibits a vicinal coupling between the olefinic protons of 16.0 cps and may therefore be assigned the *trans*-configuration in accordance with its preparation from *trans*-ferulic acid methylester (m.p.  $63-64^\circ$ ) by reduction with lithium aluminium hydride<sup>6</sup> and acetylation with acetic anhydride in

Table 1.

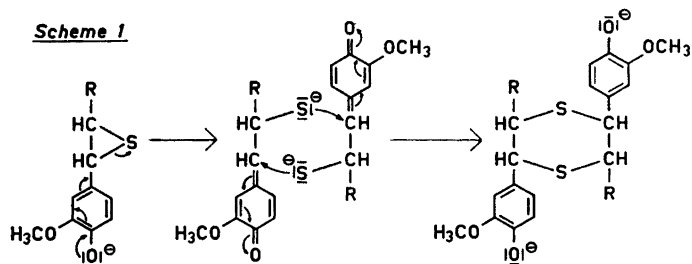
| Compound | Shifts (in ppm)    |                           |                    |                    |                     | Coupling constants<br>(in cps)   |
|----------|--------------------|---------------------------|--------------------|--------------------|---------------------|--|
|          | $\delta_{H\alpha}$ | $\delta_{H\beta}$         | $\delta_{H\beta'}$ | $\delta_{H\gamma}$ | $\delta_{H\gamma'}$ |  |
| I        | 6.68               | 5.65                      | 5.20               | —                  | —                   | $J_{\alpha\beta} = 11.0$ $J_{\beta\beta'} = 1.0$<br>$J_{\alpha\beta'} = 17.2$                          |
| IIa      | 6.42               | 5.78                      | —                  | 1.88               | —                   | $J_{\alpha\beta} = 11.5$ $J_{\alpha\gamma} = 1.8$<br>$J_{\beta\gamma} = 6.8$                           |
| IIb      | 6.34               | 5.98                      | —                  | 1.81               | —                   | $J_{\alpha\beta} = 16.0$<br>$J_{\beta\gamma} = 5.0$  |
| III      | 6.64               | 6.21                      | —                  | 4.67               | 4.67                | $J_{\alpha\beta} = 16.0$<br>$J_{\beta\gamma} = 5.8$  |
| IV       | 3.75               | 2.67                      | 3.00               | —                  | —                   | $J_{\alpha\beta} = 4.0$ $J_{\beta\beta'} = 6.0$<br>$J_{\alpha\beta'} = 2.5$                            |
| Va       | 4.03               | 3.31                      | —                  | 1.09               | —                   | $J_{\alpha\beta} = 4.0$<br>$J_{\beta\gamma} = 5.2$   |
| Vb       | 3.48               | 2.92                      | —                  | 1.36               | —                   | $J_{\alpha\beta} = 2.1$<br>$J_{\beta\gamma} = 5.0$   |
| VI       | 3.76               | 3.19                      | —                  | 4.47               | 4.02                | $J_{\alpha\beta} = 2.0$ $J_{\beta\gamma'} = 5.5$<br>$J_{\beta\gamma} = 3.4$ $J_{\gamma\gamma'} = 12.1$ |
| VII      | 3.83               | 2.54                      | 2.78               | —                  | —                   | $J_{\alpha\beta} = 5.0$ $J_{\beta\beta'} = 6.8$<br>$J_{\alpha\beta'} = 1.3$                            |
| VIIIa    | 3.78               | 3.70<br>(unre-<br>solved) | —                  | 1.26               | —                   | $J_{\alpha\beta} = 7.0$<br><br>$J_{\beta\gamma} = 6.0$   |
| VIIIb    | 3.50               | 2.99                      | —                  | 1.59               | —                   | $J_{\alpha\beta} = 5.0$<br><br>$J_{\beta\gamma} = 6.0$   |
| IX       | 3.74               | 3.22                      | —                  | 4.38               | 4.13                | $J_{\alpha\beta} = 4.8$ $J_{\beta\gamma'} = 6.8$<br>$J_{\beta\gamma} = 6.0$ $J_{\gamma\gamma'} = 12.0$ |

pyridine. The *trans*-configuration of the ferulic acid methylester of m.p. 63–64° has been shown recently.<sup>7</sup>

In epoxides the dihedral angles between vicinal ring protons are 0° for the *cis*-form and 155° for the *trans*-form.<sup>8</sup> Thus, if only geometrical factors were involved, a similar qualitative relationship between the vicinal coupling constants of the *cis*- and *trans*-forms should be expected, as is found for olefins. However, Lehn and Riehl showed recently<sup>9</sup> that a reverse qualitative relationship is generally valid for a great variety of mono- and 1,2-disubstituted ethylene oxides, the vicinal coupling constants of the *cis*-forms ( $J_{cis} = 2.5 - 5.1$  cps) being about twice those of the *trans*-forms ( $J_{trans} = 0.5 - 2.5$  cps). This inversion has been interpreted as resulting from electronic factors in the three-membered oxygen-containing ring.<sup>9</sup> The vicinal coupling constants for the epoxides IV–VI (see Table 1) fall well within the ranges given above.

In episulphides larger vicinal couplings are generally encountered than in the corresponding epoxides<sup>10</sup> (cf. also Table 1), the increase being compatible with the lower electronegativity of sulphur. As is found in epoxides, vicinal ring protons in episulphides are more strongly coupled in the *cis*- ( $J_{cis} = 6.3 - 7.1$  cps) than in the *trans*- ( $J_{trans} = 5.4 - 5.6$  cps) isomers.<sup>10</sup> The vicinal coupling constants for the episulphides VII–IX (see Table 1) agree roughly with these values.

On treatment of the episulphides (VII–IX) with 2 N sodium hydroxide at room temperature or at 100° the corresponding dithianes (X–XII) are formed. This result is in accordance with the view<sup>1</sup> that episulphide structures constitute intermediates in the cleavage of  $\beta$ -arylether linkages present in phenolic lignin units during sulphate cooking. The most plausible mechanism for this dithiane formation suggests an alkali-induced opening of the episulphide ring at the  $\alpha$ -carbon atom followed by a spontaneous dimerisation of the resulting mercapto-methylene quinone<sup>1</sup> (see Scheme 1).



An alternative pathway for the preparation of *p*-dithianes (e.g. X and XI) from olefins (I and II, respectively) was followed by reacting the corresponding dibromo compounds (XIII and XIV) with sodium sulphide. No attempt was made to isolate possible intermediates of this reaction, such as bromothiols and episulphides. The final products were obtained in relatively high yields (66.2 % and 47.6 %, respectively).

Simple aliphatic 1,2-dibromo compounds, when treated with sodium sulphide, give mainly linear polymers, the yields of *p*-dithianes being poor.<sup>11</sup> The same seems to hold true for the dibromo compound XVI in which the

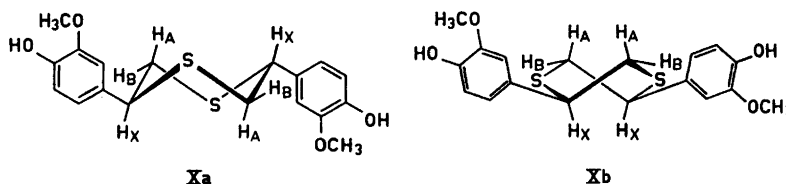
phenolic hydroxyl group in the *para*-position is blocked by methylation,<sup>12</sup> and for simple aliphatic episulphides when they are treated with sodium hydroxide.<sup>13</sup> Thus, the facile formation of *p*-dithianes from 1,2-dibromo compounds and from episulphides appears to be limited to representatives which carry a *p*-hydroxyphenyl substituent, such as compounds XIII and XIV as well as VII and VIII. This finding supports the mechanism depicted in Scheme 1.

Treatment of monoaryl-substituted episulphides with alkali afforded essentially the energetically favoured 2,5-*trans*-diaryl-*p*-dithianes (*cf.* also Ref. 1), the configurational distribution under the conditions used probably being thermodynamically controlled. However, the reaction of the dibromo compounds with sodium sulphide gives mixtures of two configurational isomers. Thus, the dibromo compound XIII yields, in addition to the 2,5-*trans*-diaryl-*p*-dithiane X (m.p. 250–250.5°),<sup>1</sup> a smaller amount of another crystalline product (m.p. 181.5–183°) showing the same analytical values. This lower melting product is evidently the *cis*-isomer of compound X. Its PMR-spectrum shows a typical ABX pattern, the chemical shifts (in ppm) and coupling constants (in cps) being similar to the corresponding values for the *trans*-form of compound X (see Table 2).

Table 2.

| Compound                              | Shifts (in ppm) |            |            | Coupling constants (in cps) |          |          |
|---------------------------------------|-----------------|------------|------------|-----------------------------|----------|----------|
|                                       | $\delta_A$      | $\delta_B$ | $\delta_X$ | $J_{AB}$                    | $J_{AX}$ | $J_{BX}$ |
| Xa ( <i>trans</i> -form)              | 3.48            | 2.95       | 4.15       | 13.3                        | 10.7     | 2.5      |
| Diacetate of Xa ( <i>trans</i> -form) | 3.54            | 3.05       | 4.28       | 13.3                        | 10.9     | 2.5      |
| Xb ( <i>skew</i> -form)               | 3.22            | 2.82       | 4.32       | 13.5                        | 10.0     | 3.0      |
| Diacetate of Xb ( <i>skew</i> -form)  | 3.20            | 2.86       | 4.36       | 14.1                        | 10.2     | 3.0      |

The coupling constants of the vicinal protons in the *trans*-form of compound X ( $J_{AX} = 10.7$ ,  $J_{BX} = 2.5$ , see Table 2) may be associated with a diaxial and an



axial-equatorial interaction, as expected for a chair conformation having both aryl substituents in the equatorial position<sup>1</sup> (Xa). The vicinal coupling constants of the *cis*-form of X ( $J_{AX} = 10.0$ ,  $J_{BX} = 3.0$ ) indicate that the dihedral angles between the vicinal protons are about the same and, thus, a similar spacial arrangement of the protons and aryl substituents as found in the *trans*-form is suggested. On these geometrical grounds the *cis*-form of compound X is assigned a stretched *skew* conformation in which the hetero atoms tend towards the median positions (Xb). Similar skew conformations of varying flexibility have been attributed recently to unsubstituted *p*-dithiane,<sup>14</sup> to exo-1,4-unsaturated cyclohexanes,<sup>14</sup> and to 2,3-dichloro-dioxane.<sup>15</sup>

### EXPERIMENTAL

All melting points are corrected. The reactions were followed by thin-layer chromatography on silica gel<sup>16</sup> using chloroform as a solvent. The different types of compounds (olefins, epoxides, episulphides, and dithianes) gave characteristically coloured spots, when the chromatograms were sprayed with 30% sulphuric acid and heated at 110° for several minutes. In the preparative runs silica gel HF<sub>254</sub><sup>16</sup> was used.

The proton magnetic resonance (PMR) spectra were recorded at 60 Mc/s on a Varian A 60 spectrometer. All spectra were run on *ca.* 10% solutions in deuteriochloroform with a small amount of tetramethylsilane added as internal reference. The shifts are reported as  $\delta$ -values in ppm.

*1-(4-Acetoxy-3-methoxy-phenyl)-1,2-dibromo-ethane (XIII)*. 1-(4-Acetoxy-3-methoxy-phenyl)-ethene (I) (11.6 g) was dissolved in chloroform (100 ml) and a solution of bromine (9.7 g) in chloroform (100 ml) was added with stirring over a period of half an hour. Evaporation of the solvent gave a white solid which was recrystallised from ligroin to yield colourless plates (18.7 g, 87.5%) m.p. 119–120°. (Found: C 37.34; H 3.73; O 13.75; Br 45.21. Calc. for C<sub>11</sub>H<sub>12</sub>O<sub>3</sub>Br<sub>2</sub>: C 37.53; H 3.44; O 13.63; Br 45.40).

*1-(4-Acetoxy-3-methoxy-phenyl)-1,2-dibromo-propane (XIV)* was prepared from 1-(4-acetoxy-3-methoxy-phenyl)-1-propene (isoeugenol acetate, II) (26 g) and bromine (20 g) as described above for compound XIII. The crude product was recrystallised once from ligroin and once from ethanol to yield thin white plates (35.5 g, 77%) m.p. 130–131°. (Found: C 39.32; H 3.92; O 13.05; Br 43.86. Calc. for C<sub>12</sub>H<sub>14</sub>O<sub>3</sub>Br<sub>2</sub>: C 39.37; H 3.85; O 13.11; Br 43.66).

*3-Acetoxy-1-(4-acetoxy-3-methoxy-phenyl)-1,2-dibromo-propane (XV)*. 3-Acetoxy-1-(4-acetoxy-3-methoxy-phenyl)-1-propene (coniferylalcohol diacetate, III)<sup>17</sup> (1.37 g) was dissolved in carbon tetrachloride (10 ml) and the solution was refluxed on a water bath whilst bromine (0.83 g) dissolved in carbon tetrachloride (10 ml) was added dropwise. The colourless residue obtained after evaporation of the solvent was triturated with ligroin and recrystallised from ethanol to yield colourless needles (1.9 g, 86.4%) m.p. 157–159°. (Found: C 39.53; H 3.85; O 18.76; Br 37.64. C<sub>14</sub>H<sub>16</sub>O<sub>5</sub>Br<sub>2</sub> requires: C 39.65; H 3.80; O 18.86; Br 37.69).

*(4-Acetoxy-3-methoxy-phenyl)-epoxy-ethane (IV)* was prepared according to the procedure described by Freudenberg and Richtzenhain<sup>18</sup> for compound V (see below). To a solution of (4-acetoxy-3-methoxy-phenyl)-ethene (I) (7.0 g) in chloroform (100 ml) was added perbenzoic acid<sup>19</sup> (4.8 g) dissolved in chloroform (100 ml). The solution was kept at 0° for two days. The benzoic acid and the excess of perbenzoic acid were removed by shaking the chloroform solution with a 2% solution of sodium carbonate (6 times) and then with water. After drying the chloroform solution was evaporated and the residue was distilled (b.p. 110–114°/0.1 mm Hg) to yield a colourless oil (5.3 g, 69.9%). (Found: C 63.84; H 6.12; O 30.41. C<sub>11</sub>H<sub>12</sub>O<sub>4</sub> requires: C 63.45; H 5.81; O 30.74).

*trans-1-(4-Acetoxy-3-methoxy-phenyl)-1,2-epoxy-propane (Vb)* was similarly prepared from *trans*-1-(4-acetoxy-3-methoxy-phenyl)-1-propene (IIb, m.p. 79.5°) (14 g) and perbenzoic acid (9.5 g). Distillation of the crude product (b.p. 128–130°/0.1 mm Hg) gave a colourless oil (12 g, 79.4%).

*cis*-1-(4-Acetoxy-3-methoxy-phenyl)-1,2-epoxy-propane (Va) was prepared analogously from *cis*-1-(4-acetoxy-3-methoxy-phenyl)-1-propene (IIa). This starting material was obtained from commercial isoeugenol by fractional distillation (removal of the *trans*-isomer)\* followed by acetylation (acetic anhydride in pyridine) and purification of the acetate (IIa) by preparative thin-layer chromatography on silica gel impregnated with a 10 % aqueous solution of silver nitrate (removal of eugenol acetate). The epoxide Va was obtained as a colourless oil in 71.4 % yield. (Found: C 64.64; H 6.63; O 28.58. C<sub>12</sub>H<sub>14</sub>O<sub>4</sub> requires: C 64.85; H 6.35; O 28.80).

3-Acetoxy-1-(4-acetoxy-3-methoxy-phenyl)-1,2-epoxy-propane (VI) was obtained from 3-acetoxy-1-(4-acetoxy-3-methoxy-phenyl)-1-propene (III) (2.35 g) by treatment with perbenzoic acid at 0° for one week. After purification by means of preparative thin-layer chromatography the resulting oil (2.7 g) crystallised on standing in a refrigerator for a week. Recrystallisation from chloroform-hexane yielded colourless needles (2.06 g, 73.5 %) m.p. 73–74.5°. (Found: C 60.02; H 5.67; O 34.10. C<sub>14</sub>H<sub>16</sub>O<sub>6</sub> requires: C 59.99; H 5.75; O 34.25).

*trans*-1-(4-Acetoxy-3-methoxy-phenyl)-1,2-epithio-propane (VIIIb) was obtained by treating the corresponding *trans*-epoxide (Vb) (2.6 g), dissolved in methanol (50 ml), with thiourea (1.1 g, 1.5 mol)<sup>19</sup> at room temperature. After 2 days, ice-water (80 ml) was added and the methanol was removed *in vacuo* at a temperature not exceeding 25°. The residue was then extracted with chloroform and the chloroform layer was dried with anhydrous sodium sulphate. Evaporation of the solvent yielded a slightly yellow oil (2.5 g) which proved difficult to purify. Besides some unreacted epoxide it contained about 25 % of the corresponding olefin (IIb) calculated from the integrated signals of the methyl protons in the PMR spectrum. Neither distillation in a high vacuum nor purification by preparative thin-layer chromatography was effective because of the tendency of the episulphide to undergo desulphurisation. The yield of the slightly impure product after several separations on silica gel plates of 1 mm thickness was 1.4 g, 50.3 %. Found: C 61.37; H 5.64; O 21.25; S 12.20. C<sub>12</sub>H<sub>14</sub>O<sub>3</sub>S requires: C 60.48; H 5.92; O 20.14; S 13.46).

*cis*-1-(4-Acetoxy-3-methoxy-phenyl)-1,2-epithio-propane (VIIIa) was similarly obtained by treating the *cis*-epoxide (Va) (0.22 g, 3 mmoles) at room temperature for one week. Repeated purification by preparative thin-layer chromatography afforded a colourless oil in a poor yield (12 %).

(4-Acetoxy-3-methoxy-phenyl)-epithio-ethane (VI). (4-Acetoxy-3-methoxy-phenyl)-epoxy-ethane (IV) (2.0 g) treated with thiourea and worked up as described above yielded the episulphide VI (1.9 g, 88.1 %) as a colourless oil. (Found: C 59.45; H 5.95; O 20.98; S 13.78. C<sub>11</sub>H<sub>12</sub>O<sub>3</sub>S requires: C 59.45; H 5.39; O 21.40; S 14.30).

*trans*-3-Acetoxy-1-(4-acetoxy-3-methoxy-phenyl)-1,2-epithio-propane (IX) was analogously prepared from the epoxide IX (2.0 g) and thiourea (0.32 g). After purification by preparative thin-layer chromatography the product crystallised when kept in a refrigerator for several days. Recrystallisation from isopropyl ether yielded colourless needles (1.7 g, 80.4 %) m.p. 68–70°. (Found: C 56.96; H 5.50; O 27.22; S 10.60. C<sub>14</sub>H<sub>16</sub>O<sub>6</sub>S requires: C 56.74; H 5.44; O 27.00; S 10.82).

2,5-Di-(4-hydroxy-3-methoxy-phenyl)-p-dithiane (X).

a) from (4-acetoxy-3-methoxy-phenyl)-epithio-ethane (VII). The episulphide VII (0.35 g) was dissolved in ethanol (2 ml) and to this solution was added 2 N sodium hydroxide (10 ml). The mixture was heated on a boiling water bath whilst nitrogen was passed through the solution. Working up after one hour as described previously (see Ref. 1) afforded the *p*-dithiane X (0.20 g, 70.4 %), m.p. 249–250°, identical with the compound obtained by treatment of 1-*S*-acetyl-1-(4-hydroxy-3-methoxy-phenyl)-2-*O*-(2-methoxy-phenyl)-1-monothioethyleneglycol with 2 N sodium hydroxide<sup>1</sup> (analyses, mixed m.p., PMR spectra).

When the episulphide VII (0.08 g) was treated with 2 N sodium hydroxide at room temperature under otherwise identical conditions the dithiane X (0.053 g) was obtained in 80.1 % yield, m.p. 243–246°.

b) from 1-(4-acetoxy-3-methoxy-phenyl)-1,2-dibromo-ethane (XIII). The dibromo compound XIII (46.0 g) was treated with a solution of Na<sub>2</sub>S.9 H<sub>2</sub>O (157 g) in 50 %

\* We thank Drs. G. Aulin-Erdtman and Y. Tomita, Träkemiska institutionen, Kungl. Tekniska Högskolan, Stockholm, for a sample of this distillate.

aqueous ethanol (200 ml) on a boiling water bath whilst nitrogen was passed through the solution. After 16 h the reaction mixture was placed in a refrigerator and allowed to crystallise. Centrifuging, washing with water and treating with dilute hydrochloric acid as described earlier<sup>1</sup> afforded a crystalline product which was heated with a small amount of ethanol (80 ml). The residue was filtered off and recrystallised from ethanol to yield *trans*-2,5-di-(4-hydroxy-3-methoxy-phenyl)-*p*-dithiane (Xa) (13.3 g, 55.8%), m.p. 247–250°. The product was found to be identical with the *p*-dithiane prepared from the episulphide VII (mixed m.p.).

Evaporation of the filtrate (see above) and recrystallisation of the resulting colourless residue from either 1-butanol or chloroform-hexane afforded colourless needles (2.5 g, 10.4%, m.p. 181.5–183°. This compound exhibited a PMR spectrum similar to that of the *trans*-form of X (see Table 2) indicating a flexible *skew* conformation of the 2,5-di-(4-hydroxy-3-methoxy-phenyl)-*p*-dithiane. (Found: C 59.96; H 5.20; O 17.86. C<sub>18</sub>H<sub>20</sub>O<sub>4</sub>S<sub>2</sub> requires: C 59.34; H 5.49; O 17.57; S 17.61). Acetylation with acetic anhydride in pyridine and recrystallisation of the resulting diacetate from chloroform-hexane gave *skew*-2,5-di-(4-acetoxy-3-methoxy-phenyl)-*p*-dithiane as colourless plates, m.p. 163–164°. (Found: C 58.96; H 5.04; O 21.33; S 14.53. C<sub>22</sub>H<sub>24</sub>O<sub>6</sub>S<sub>2</sub> requires: C 58.93; H 5.35; O 21.41; S 14.30).

*2,5-Di-(4-hydroxy-3-methoxy-phenyl)-3,6-dimethyl-p-dithiane (XI).*

a) from *trans*-1-(4-acetoxy-3-methoxy-phenyl)-1,2-epithio-propane (VIIIb). The episulphide VIIIb (0.40 g), when treated with 2 N sodium hydroxide in the manner described for the preparation of dithiane X (see above), gave the dithiane XI (0.13 g, 39.5%), m.p. 183–186°.

b) from 1-(4-acetoxy-3-methoxy-phenyl)-1,2-dibromo-propane (XIV). A solution of the dibromo compound V (10 g) in ethanol (70 ml) was slowly added to a solution of Na<sub>2</sub>S<sub>2</sub>O<sub>9</sub>·9 H<sub>2</sub>O (33.8 g) in water (100 ml). The mixture was heated on a boiling water bath for 24 h and then kept at 0° for several days. The precipitate formed was centrifuged off, washed with water, dried over P<sub>2</sub>O<sub>5</sub> and recrystallised three times from acetic acid and once from chloroform-hexane to yield colourless needles (2.56 g, 47.6%), m.p. 185–187° (not sharp). The elemental analyses were in good agreement with those calculated for compound XI. (Found: C 61.01; H 6.00; O 16.35; S 16.21. C<sub>20</sub>H<sub>24</sub>O<sub>4</sub>S<sub>2</sub> requires: C 61.19; H 6.16; O 16.30; S 16.34). The signals of the methyl protons in the PMR spectrum and the thin-layer chromatogram indicated that the product was a mixture of essentially two components probably corresponding to the two forms of compound X (see above).

*2,5-Di-(4-hydroxy-3-methoxy-phenyl)-3,6-dihydroxymethyl-p-dithiane (XII).* *trans*-3-acetoxy-1-(4-acetoxy-3-methoxy-phenyl)-1,2-epithio-propane (IX) (0.35 g) was dissolved in dioxane (10 ml) and to the solution was added 2 N sodium hydroxide (10 ml) with stirring at room temperature. After 36 h the reaction mixture was poured into 0.5 N hydrochloric acid precooled to 0°. The mixture was kept in a refrigerator for 36 h. The precipitate formed (0.10 g) was filtered off. From the mother liquor additional dithiane XII (0.11 g, total yield 83.9%) was isolated by extracting with a mixture of ethanol and chloroform (1:5). The crude material was triturated with chloroform to yield a product melting between 142 and 147°. Attempts to purify it by recrystallisation were unsuccessful. Acetylation with acetic anhydride in pyridine gave a tetraacetate (m.p. 148–150°) identical with the tetraacetate prepared by treating 3-*O*-acetyl-1-*S*-acetyl-1-(4-hydroxy-3-methoxy-phenyl)-2-*O*-(2-methoxy-phenyl)-1-monothioglycerol with 2 N sodium hydroxide and acetylation of the resulting *p*-dithiane with acetic anhydride in pyridine<sup>1</sup> (mixed m.p.).

Attempts to prepare the *p*-dithiane XII by treating the dibromo compound XV with an aqueous solution of sodium sulphide in the manner described above were unsuccessful.

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