

The Reactions of Lignin During Neutral Sulphite Cooking

Part II.* The Behaviour of Phenylcoumaran Structures

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Part I of this series dealt with the reactions of model compounds representing structural elements of the β -arylether type in lignin under the conditions of neutral sulphite cooking. The present communication describes the behaviour of the cyclic benzylaryl ether I, dihydro-dehydro-diisoeugenol,² and its methyl ether II,³ models of the dimeric units of the phenylcoumaran type.

A solution of compound I (2.0 g) in freshly prepared neutral sulphite "cooking liquor" (pH 7, 80 ml) containing 0.5 moles of sodium bisulphite per litre of water was heated for 3 h at 180°. Extraction of the solution with chloroform removed the starting material and a stilbene (main chloroform-soluble reaction product), as well as traces of two further components, probably demethylation products. The latter were separated from the rest of the chloroform extract by preparative thin-layer chromatography on silica gel HF₂₅₄ using chloroform-acetone (9:1) as solvent. The remaining components (starting material and stilbene) were acetylated with acetic anhydride-pyridine (1:1) and the resulting acetates were separated also by thin-layer chromatography using benzene-chloroform (3:2) as moving phase (run four times).

trans-2,4'-Diacetoxy-3,3'-dimethoxy-5-propyl- α -methyl-stilbene (IV) was obtained in 22% yield and recrystallised from ethanol, m.p. 111–112° (lit.⁹ 111–112°). (Found: C 69.80; H 6.92; O 23.41. Calc. for C₂₆H₂₈O₆: C 69.92; H 6.79; O 23.29). The NMR-spectrum in deuterio-chloroform (100 Mc, internal reference: tetramethyl-silane) revealed the *trans*-configuration of the compound, the protons of the α -methyl group exhibiting a well resolved doublet ($J=1.6$ cps), centered at 2.15 ppm, which is due to transoid allylic coupling with

the olefinic proton (cf. Ref. 4). For the corresponding transoid allylic coupling constant of the methyl protons in *cis*-isoeugenol the same value (1.6 cps) was reported,⁵ whereas the cisoid allylic coupling constant for the methyl protons in *trans*-isoeugenol was found to be less than 0.5 cps.⁵

The aqueous solution after extraction with chloroform was passed over a cation exchange resin of type Dowex 50W-X8 (in the H⁺-form) and saturated with nitrogen to remove sulphur dioxide. A small sample of the eluate was used for paper chromatographic investigation (Whatman No. 3 paper, solvent: ethanol-conc. ammonia-water (12:1:3)). The rest of the acidic solution was neutralised with barium hydroxide. The precipitate of barium sulphate was filtered off and the filtrate was evaporated to dryness. Acetylation of the residue with acetic anhydride-pyridine (1:1) afforded a mixture of acetylated barium sulphonates which by cation exchange followed by neutralisation with silver oxide was converted into the corresponding acetylated silver sulphonates. The latter were reacted with methyl iodide in acetonitrile⁶ yielding a mixture of the corresponding methyl esters which were separated by preparative thin-layer chromatography on silica gel HF₂₅₄ using benzene-ethyl acetate (9:1) as solvent (run twice). Two stereoisomeric α -sulphonic acid methylesters (VI) were isolated and identified by elemental analyses and NMR spectra.

erythro-(2,4'-Diacetoxy-3,3'-dimethoxy-5-propyl- α -methyl)-bibenzyl- α' -sulphonic acid methylester (VI) was obtained as colourless crystals which after recrystallisation from ethanol melted between 127 and 129°. (Found: C 58.90; H 6.33; O 28.46; S 6.41. C₃₅H₃₂O₉S requires: C 59.07; H 6.29; O 28.33; S 6.31). The NMR spectrum (see above) shows a strong vicinal coupling of the benzylic proton giving rise to a doublet centered at 4.57 ppm ($J=11$ cps). This large coupling constant indicates the thermodynamically more stable *erythro*-form of the compound having a *trans*-arrangement of the α - and β -protons.⁷ The value is in good agreement with the constants of the spin coupling between the protons attached to carbon atoms 2 and 3 of the coumaran ring in dihydro-dehydro-diisoeugenol acetate (I, R=CH₃-CO) and in dehydro-diisoeugenol (9.5 and 9.8 cps, respectively).⁸ For the latter the *trans*-configuration was proved by ozonolysis and isolation of *erythro*- β -methyl malic acid.⁵

threo-(2,4'-Diacetoxy-3,3'-dimethoxy-5-propyl- α -methyl)-bibenzyl- α' -sulphonic acid methylester (VI) was isolated as colourless crystals melting at 126.5–127.5° after re-

* Part I, see Ref. 1

crystallisation from ethyl acetate-hexane. The melting interval after admixture of the *erythro*-form (see above) was 104–110°. The total yield of the *erythro*- and *threo*-forms of compound VI was about 46 %, their ratio being approximately 3:1. (Found: C 59.15; H 6.46; O 28.36; S 6.34. $C_{25}H_{32}O_9S$ requires: C 59.07; H 6.29; O 28.33; S 6.31).

The *threo*-configuration with a *cis*-arrangement of the α - and β -protons was ascribed to this compound on the basis of the weak vicinal coupling of the benzylic proton (a doublet, $J=3$ cps, as compared with $J=11$ cps for the corresponding coupling of the α - and β -protons in the *erythro*-form, see above). The integrals and chemical shifts of the NMR-signals of the remaining protons in compound IV and in both forms of compound VI were also in agreement with the proposed structures.

In addition to the two stereoisomers of compound VI a small amount of methane sulphonic acid was formed (*cf.* also Ref. 1). This was identified in the water-soluble fraction by paper chromatography (see above).

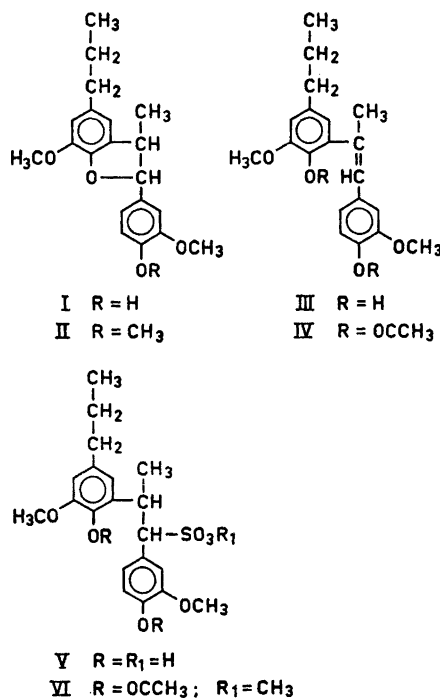
The extent of reaction of compound I with neutral sulphite, when calculated either from the yields of isolated and identified reaction products or from the amount of recovered starting material, was about 70 %.

The methyl ether of compound I (II) was essentially unchanged after the treatment with neutral sulphite and could be recovered in almost quantitative yield. Only traces of methane sulphonic acid and of two other sulphonic acids, probably identical with the two forms of V, (formed *via* partial demethylation of II to I) could be detected (paper chromatography, see above).

For the sake of comparison, compounds I and II (2 g of each) were also subjected to treatment under the conditions of acidic sulphite cooking (heating to 135° in an acidic sulphite solution of pH 1.5 (80 ml), containing 6.23 % total SO_2 , for 7 h).

In contrast to the extensive cleavage reaction brought about by neutral sulphite (see above), acidic sulphite did not attack the cyclic α -arylether bond in the phenolic phenylcoumaran I to any appreciable degree. Only traces of sulphonic acids, indistinguishable from the two forms of compound V by paper chromatography, were formed and the starting material could be recovered from the chloroform extract in high yield.

The same result was obtained with the methylether of I (II) which on treatment with acidic sulphite solution remained essentially unaffected.



Thus, the α -arylether linkage in phenolic units of the phenylcoumaran type (*e.g.* in compound I) is cleaved extensively by neutral sulphite giving rise to the corresponding *o,p'*-dihydroxy-stilbene structure (*e.g.* III) and α -sulphonic acid structure (*e.g.* V) Etherification of the phenolic hydroxyl group in structural units of type I blocks this cleavage reaction almost completely.

This behaviour of the α -arylether bond in phenolic and non-phenolic units of the phenylcoumaran type towards neutral sulphite is reminiscent of the behaviour of the β -arylether bond in phenolic and non-phenolic units of the β -arylether type.¹ Both these types of arylether linkages (α and β), when present in phenolic phenylpropane units, are extensively cleaved by neutral sulphite but remain essentially unaffected on treatment with acidic sulphite.

The cleavage of α -arylether bonds in phenolic units of the phenylcoumaran type by neutral sulphite and the stability of these bonds in non-phenolic units towards

the same reagent is analogous to the situation prevailing in alkali⁹ and sulphate^{10,11} cooking, where phenolic α -arylether structures of the phenylcoumaran type also gave *o,p'*-dihydroxy-stilbene structures, whereas non-phenolic units of the same structural type proved stable.

During sulphate cooking, the cleavage of the α -arylether bond in phenolic phenylcoumaran structures carrying a hydroxymethyl group on the hydrofuran ring (instead of a methyl group as in compound I) is accompanied by a loss of the hydroxymethyl group (presumably as formaldehyde)¹¹. It appears that an analogous elimination of formaldehyde also takes place during neutral sulphite cooking⁸ (cf. also Ref. 1).

The formation of methane sulphonic acid during neutral sulphite treatment of methoxyl-containing model compounds of the α - and β ¹-arylether types and of isolated lignins⁸ further parallels the results of sulphate cooking. Subjected to the conditions of the latter process, methoxyl-containing model compounds¹² and lignins¹³ are partially demethylated with formation of methyl mercaptan and dimethyl sulphide.

The splitting of the α -arylether bond in phenolic phenylcoumaran units and the cleavage of methylether linkages increase the content of phenolic hydroxyl groups and, thus, together with the sulphonation in α -position, facilitate the dissolution of lignin without contributing to its degradation. Apparently, the findings that *o,p'*-dihydroxy-stilbene structures are formed from phenolic phenylcoumaran units and that they are photochemically and thermally converted into potential chromophoric systems¹⁴ provide a possible explanation for some of the colour characteristic of neutral sulphite pulps.

The mechanisms of the cleavage of arylether linkages by neutral sulphite are currently being studied.

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Enolization of Ketones

VII.¹ The Effect of Solvent on the Orientation of Acid-Catalyzed Deuterium Exchange in 2-Butanone

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The application of NMR technique to the measurements of deuterium exchange in ketones allows the direct observation of the rate of deuterium uptake at the two positions α - to the carbonyl function, and in the special case of unsymmetric ketones in which both sets of α -protons are distinguishable and exchangeable, permits the calculation of the thermodynamic param-

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