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The Reactions of Lignin during Sulphate Cooking

IX.* Interaction between Thiol Groups and Intermediary Epoxide Structures

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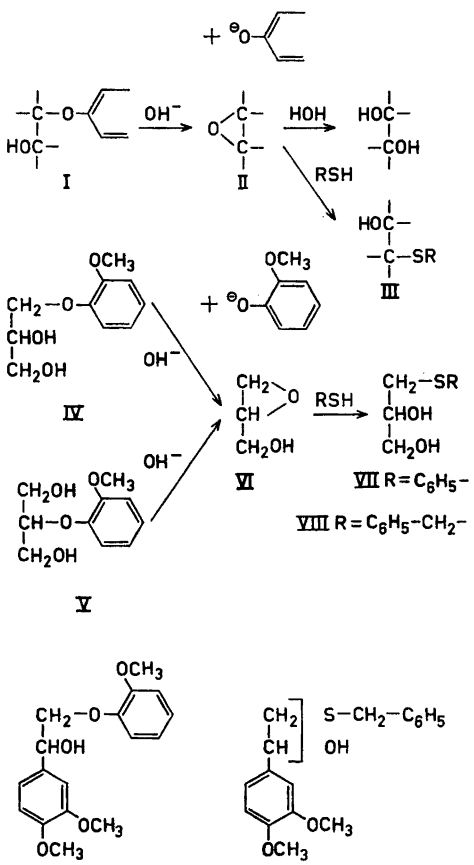
During sulphate cooking sulfhydryl groups are introduced into lignin. Of the possible pathways of introduction, the addition of sulphide ions present in the cooking liquor to methylene quinone structures formed during the cooking procedure appears to be the most important one.[1] The resulting benzylthiol groups were shown in model studies to enhance the alkaline splitting of neighbouring (= β) arylether bonds by intramolecular nucleophilic displacement with formation of 1,2-episulphide structures.[1]

In the present communication we wish to report on model experiments illustrating another type of reaction in which thiol groups may be involved during sulphate cooking.

The alkaline splitting of β-hydroxyalkylarylether bonds (I) was previously shown to proceed *via* 1,2-epoxide structures (II).[2,3] It could be anticipated that these structures will be attacked by the strongly nucleophilic thiol groups to yield β-hydroxyalkylsulphides (III). When the



* Part VIII, see Ref. 1.

alkaline cleavage of β-hydroxyalkyl-arylethers (I) was carried out in the presence of thiols, the expected hydroxy-sulphides (III) were formed. The formation of these hydroxysulphides, apart from showing a possible reaction of thiol groups introduced into lignin during sulphate cooking, further supports the proposed [2,3] course of the alkaline splitting of β-hydroxyalkyl-arylether structures (I) *via* the corresponding epoxide structures (II).

1-S-Phenyl-1-monothioglycerol (VII). A solution of compound IV (2.0 g) in 2 N sodium hydroxide (60 ml) containing thiophenol (1.5 g) was placed in a reaction vessel of stainless steel. The air in the reaction vessel was carefully replaced by nitrogen and the sample was rotated in a polyglycol bath (170°) for 2 h. The warming up period from room temperature to 170° took about 2.5 h. After cooling, the reaction mixture was extracted with chloroform and the combined chloroform extracts were dried (Na_2SO_4) and evaporated. The solid residue was recrystallised from benzene yielding the thiophenylether VII (1.0 g, 53.5 %), m.p. 66.5–67.5°, mixed m.p. with an authentic sample prepared according to Ref. 4 showed no depression. (Found: C 58.80; H 6.59; O 17.12; S 17.14. Calc. for $C_9H_{12}O_2S$: C 58.70; H 6.52; O 17.38; S 17.41).

Under the conditions mentioned above compound V gave the same thiophenylether (VII) (m.p. and mixed m.p.) in 50 % yield. The thiophenylether (VII) was also obtained by reacting equimolar amounts of the common intermediate (glycidol, VI) and thiophenol.

1-S-Benzyl-1-monothioglycerol (VIII). Compound IV, when treated with 2 N sodium hydroxide in the presence of benzylmercaptan in a similar manner, yielded an oil, from which the thiobenzylether VIII was isolated by preparative chromatography on layers of silica gel HF254 [5] of 1 mm thickness using chloroform as solvent (oil, yield 33 %). (Found: C 60.55; H 7.12; O 16.23; S 15.88. $C_{10}H_{14}O_2S$ requires: C 60.61; H 7.07; O 16.15; S 16.18).

The same thiobenzylether (VIII) was obtained (analysis, thin-layer chromatography), when compound V was treated with sodium hydroxide in the presence of benzylmercaptan under similar conditions or when epoxide VI was reacted with benzylmercaptan.

The location of the thiophenyl and thiobenzyl groups in compounds VII and VIII, respectively, was established by periodate oxidation. Two moles of periodate were consumed per mole of compound VII and VIII, one mole for conversion of the sulphide group to the sulphoxide group [6] and the other for oxidation of the 1,2-glycol group. The product arising from periodate oxidation of compound VII was isolated by extraction of the evaporated oxidation mixture with ethanol, purified by preparative thin-layer chromatography and identified as its 2,4-dinitrophenylhydrazone. *Phenylsulphinyl-acetaldehyde-2,4-dinitrophenylhydrazone* was obtained as yellow needles melting at 172–173°. (Found: C 48.03; H 3.65; O 23.14; N 15.93; S 9.05. $C_{14}H_{12}O_5N_4S$ requires: C 48.25; H 3.48; O 22.98; N 16.09; S 9.21). Benzyl-sulphinyl-acetaldehyde formed from compound VIII turned out to be unstable and could not be purified and characterised in the manner described above.

1-(3,4-Dimethoxyphenyl)-ethyleneglycol-2-guaiacylether (IX) on treatment with 2 N sodium hydroxide in the presence of benzylmercaptan under the conditions mentioned above gave a complex mixture of reaction products containing two chromatographically similar compounds which were separated with great losses by preparative thin-layer chromatography (yields about 50 mg of each). The analytical values were in agreement with those calculated for dimethoxyphenyl-monothioethyleneglycol-benzylethers (probably 1- and 2-isomers, X and XI). (Found: C 67.14; H 7.03; O 15.92; S 11.27; and C 66.85; H 6.75; O 15.82; S 10.40. $C_{17}H_{20}O_3S$ requires: C 67.11; H 6.57; O 15.78; S 10.54).

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