

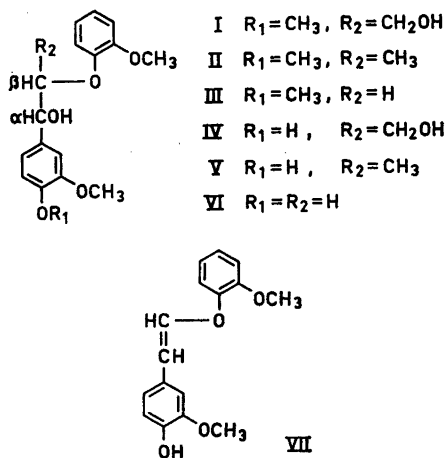
The Behaviour of Lignin in Alkaline Pulping

II. Model Experiments with Arylalkyl- β -aryl Ethers *

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Analytical studies of lignin¹ as well as work regarding its enzymatic synthesis² have clearly demonstrated the arylglycerol- β -aryl ether structure to be one of the major linking principles in lignin. The behaviour of model compounds containing the " β -aryl ether" linkage on heating with 2 N NaOH (170°), *i.e.*, under the conditions of the "soda pulping" of wood, was studied by Gierer and co-workers.³



Non-phenolic models, such as I–III, were found to undergo α,β -epoxide formation with simultaneous removal of the β -aroxyl substituent as guaiacol. The phenolic compounds IV and VI, however, were converted in moderate yields, probably *via* the

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corresponding quinone methides, to the β -enol aryl ether VII. The formation of VII from the glycerol derivative IV involves, in addition to the loss of 1 mole of H_2O , the removal of the terminal methylol group (as formaldehyde). The latter reaction was also encountered in this laboratory in the "sulphate cooking" of dihydro-dehydro-diconiferyl alcohol (see preceding communication⁴).

In connection with the last-mentioned study,⁴ the behaviour of the phenolic β -aryl ethers IV, V, and VI under the conditions of "sulphate pulping" (= "kraft pulping") of wood (cooking liquor containing Na_2S in addition to NaOH, 170°) was investigated (nitrogen atmosphere). Considerable β -ether fission was observed in all three cases, guaiacol being formed in yields of about 50, 80, and 70 %, respectively. (The guaiacol was extracted with dichloromethane from the neutralized reaction mixtures and purified by chromatography on a silica gel column with dichloromethane as eluant. It was identified by its IR spectrum and determined quantitatively by UV spectrophotometry.) In addition, compounds IV and VI were found to give small amounts of the enol aryl ether VII of Gierer and Norén,^{5a} who detected this product — but no guaiacol — in their experiments carried out in the absence of Na_2S .

Comparison of the results reported by Gierer and Norén⁵ with those obtained in our laboratory seemed to indicate that the presence of sulphide ions in the alkaline cooking liquor favoured the cleavage of the β -aryl ether linkages present in the phenolic models. Comparative experiments with 2 N NaOH and with a mixture of NaOH and Na_2S (3.5 g NaOH and 3.1 g $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ per 100 ml of water) were therefore carried out. Although guaiacol was found to be formed from IV and VI with both cooking liquors, the yields of guaiacol obtained in sodium hydroxide alone (20 and 30 %, respectively) were less than half those obtained in the sulphide-containing system (50 and 70 %, respectively). In both systems guaiacol formation was practically finished after 1 h at 170°. Furthermore, guaiacol was liberated in both systems from the enol aryl ether VII much more slowly (about 10 % after 4 h at 170°) than from IV and VI, which shows that VII is not an intermediate in the β -ether cleavage reactions of IV and VI. The β -aryl ether cleavage and the formation of the comparatively alkali-stable enol ether VII are competitive reactions, the

former reaction being markedly favoured by sulphide ions (cf. also Enkvist *et al.*⁵).

Gierer *et al.*,⁶ in recent work arrived at similar conclusions and also discussed the mechanisms involved in both types of reactions.

The model experiments reported so far support the view that the alkaline dissolution of lignin from wood is due mainly to the cleavage of various types of alkyl aryl ether linkages. Among these reactions the fission of dimeric elements of the non-phenolic arylglycerol- β -aryl ether type (cf. model compound I, R₁ = α - or β -C atom of next side-chain) seems to be independent of the presence of sulphide ions,^{6b} however, in similar structures carrying a free phenolic hydroxyl (cf. model compound IV) β -ether cleavage becomes extensive only in the presence of sulphide ions. Since a certain number of such phenolic groups is initially present in lignin and further amounts are liberated in the course of the alkaline cooking processes, sulphide ions will be expected to favour the fragmentation of the lignin. This seems to explain, at least partially, the relative ease at which delignification of wood takes place in kraft cooking as compared to soda cooking.

Very little is known as yet regarding the fate of the side-chain of the phenolic units to which the β -aryl ether grouping was attached. Preliminary results indicate that "kraft cooking" of model compound IV, in addition to guaiacol gives appreciable amounts of carboxylic acids. Obviously, the formation of carboxyl groups would further contribute to the solubilization of lignin in kraft pulping of wood.

Preparation of model compounds. For the preparation of IV see Ref.⁸ Compound VI, also reported by Gierer and Norén,^{3a} was obtained from ω -(2-methoxyphenoxy)-aceto-guaiacone benzoate^{8a} on treatment with NaBH₄ in 0.1 N methanolic NaOH. Yield 90 %, m.p. 129–130°.

The syntheses of II and V will be described in a forthcoming paper.

1. Adler, E. *Paper and Timber (Finland)* **43** (1961) 634; Kratzl, K. *Ibid.* **643**; Lundquist, K. *Acta Chem. Scand.* **16** (1962) 2303.
2. Freudenberg, K. *Fortschr. Chem. org. Naturstoffe* **20** (1962) 41.
3. a) Gierer, J. and Norén, I. *Acta Chem. Scand.* **16** (1962) 1713; b) *Ibid.* 1976; c)

* We thank Dr. Gierer for communicating these results to us prior to publication.

- Gierer, J., Lenz, B., Norén, I. and Söderberg, S. *Tappi* **47** (1964) 233.
4. Adler, E., Marton, J. and Falkehag, I. *Acta Chem. Scand.* **18** (1964) 1311.
 5. Enkvist, T., Ashorn, T. and Hästbacka, K. *Paper and Timber (Finland)* **44** (1962) 395.
 6. a) Gierer, J. and Smedman, L. Å. *Acta Chem. Scand.* **18** (1964) 1244; b) Gierer, J., Lenz, B. and Wallin, N.-H. *Ibid.* **18** (1964). *In press.*
 7. Freudenberg, K., Harkin, J. M. and Werner, H.-K. *Chem. Ber.* **97** (1964) 909.
 8. a) Adler, E. and Eriksoo, E. *Acta Chem. Scand.* **9** (1955) 341; b) Kratzl, K., Kisser, W., Gratzl, J. and Silbernagel, H. *Monatsh.* **90** (1959) 771.

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III. Fragmentation of Björkman Lignin

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As reported in Part II,¹ the alkaline cleavage of the alkyl aryl ether bond in lignin model compounds of the guaiacylglycerol- β -guaiacyl ether type is favoured by the presence of sodium sulfide. Gierer *et al.*² discussed the mechanism of the ether cleavage reactions involved (cf. also Enkvist *et al.*³). These model experiments indicate that more extensive degradation of lignin occurs in "kraft pulping" (NaOH + Na₂S) than in "soda pulping" (NaOH) of wood, which may explain the greater ease at which delignification takes place in the first-mentioned process.

Spruce lignin isolated according to Björkman (= "milled wood lignin") was now subjected to heating with aqueous NaOH with and without the addition of Na₂S, and the degree of fragmentation was examined by studying the behaviour of the reaction products on a Sephadex column. "Gel filtration" through Sephadex columns has been used for the fractionation of aqueous mixtures of solutes in the order of their molecular weights ("molecular