

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

Gierer *et al.*,<sup>6</sup> 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- $\beta$ -aryl ether type (cf. model compound I, R<sub>1</sub> =  $\alpha$ - or  $\beta$ -C atom of next side-chain) seems to be independent of the presence of sulphide ions,<sup>6b</sup> however, in similar structures carrying a free phenolic hydroxyl (cf. model compound IV)  $\beta$ -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  $\beta$ -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.<sup>8</sup> Compound VI, also reported by Gierer and Norén,<sup>3a</sup> was obtained from  $\omega$ -(2-methoxyphenoxy)-aceto-guaiacone benzoate<sup>3a</sup> on treatment with NaBH<sub>4</sub> 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.

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

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## The Behaviour of Lignin in Alkaline Pulping

### III. Fragmentation of Björkman Lignin

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As reported in Part II,<sup>1</sup> the alkaline cleavage of the alkyl aryl ether bond in lignin model compounds of the guaiacylglycerol- $\beta$ -guaiacyl ether type is favoured by the presence of sodium sulfide. Gierer *et al.*<sup>2</sup> discussed the mechanism of the ether cleavage reactions involved (cf. also Enkvist *et al.*<sup>3</sup>). These model experiments indicate that more extensive degradation of lignin occurs in "kraft pulping" (NaOH + Na<sub>2</sub>S) 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 Na<sub>2</sub>S, 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

sieving").<sup>4</sup> The gel material, however, exhibits considerable adsorption affinity towards aromatic compounds, which delays elution and disturbs the molecular sieving effect.<sup>5,4</sup>

It has now been found<sup>6</sup> that adsorption of aromatic solutes is greatly decreased if certain polar organic solvents or their mixtures with water are used as gel-swelling agents and as eluents. In comparative experiments with Björkman lignin ( $\bar{M}_w$  7000–11000<sup>7</sup>) and two kraft lignins ( $\bar{M}_w$  3500 and 2900),\* these three products, on elution with dimethylsulfoxide (DMSO), behaved as was expected on the basis of their molecular weights. In the present experiments DMSO was chosen.

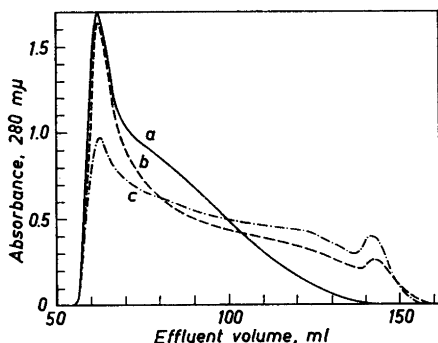


Fig. 1. Elution curves obtained on gel filtration (Sephadex G50F) of Björkman spruce lignin (a) and its alkaline degradation products (b, c). See text for experimental conditions.

Fig. 1 shows the results of the gel filtration of untreated Björkman lignin (curve a) and of the reaction products obtained from this lignin on heating with 1 M NaOH ("soda cook", curve b), and with a "kraft cooking" liquor (0.89 M NaOH + 0.11 M Na<sub>2</sub>S, curve c). The concentration of material in the effluent was followed by measuring the light absorption at 280 mμ.

The absorption peak at the beginning of elution curve a corresponds to the most rapidly eluted portion of Björkman lignin, the molecular weight of which is too high to permit the molecules to enter the gel particles; the lower-molecular weight por-

tion is retarded and eluted gradually. "Soda cooking" (curve b) apparently brings about degradation of the latter portion only. In "kraft cooking", however, the high-molecular weight lignin portion is also broken down (curve c). According to model experiments, the peaks at the right hand end of the elution curves b and c correspond to monomeric material such as acetoguaiacone and vanillin. The separation of fractions containing monomeric and dimeric material, respectively, by gel filtration, and the isolation of individual degradation products is being studied in this laboratory.<sup>8</sup>

Fig. 1 demonstrates that the alkaline fragmentation of lignin is enhanced by sulfide ions ("kraft process"). This may be mainly due to the enhancement of β-aryl ether cleavage demonstrated in model experiments.<sup>1,2</sup>

**Experimental.** Solutions of Björkman lignin (0.3 g) in the two cooking liquors (7 ml; see compositions above) were heated at 130° for 1.5 h. Acidification of the diluted reaction mixture gave a brownish yellow precipitate (A) which was centrifuged off and washed with water. The combined aqueous phase and washings were concentrated to a volume of 10 ml, from which organic material was recovered by addition of dioxane (10 ml) followed by repeated extraction with chloroform. The yellow oil remaining after evaporation of the chloroform solution and precipitate A were dissolved together in DMSO (30 ml).

A 2 ml-sample of the solution was brought onto a column (22 × 470 mm) of Sephadex G50F, which had been swollen in DMSO, and elution with the same solvent carried out at a rate of 30 ml/h. The absorbance of the effluent, collected in 5 ml-fractions, was continuously recorded with a Beckman DB spectrophotometer equipped with a 1 mm flow cell, a Sargent recorder, and a device which marked the shifts of the fraction tubes.

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## On the Separation of Lignin Degradation Products\*

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As reported earlier,<sup>1</sup> 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone (I) has been isolated from spruce Björkman lignin after 4 hours' reflux with 0.2 M HCl in dioxane-water 9:1 ("acidolysis"). Vanillin, coniferyl aldehyde, and 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone were also shown to be formed. Finally, the reaction mixture was found to contain a compound which was assumed to be 1-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-2-propanone. The correctness of this assumption has now been confirmed by comparison with a synthetic sample obtained according to Gardner *et al.*<sup>2</sup>

Improvement of the separation methods, especially the use of gel filtration, has resulted in the detection of further degradation products, some of which have been isolated in a pure state.

From the crude, very complex mixture of acidolysis products, the major part of polymeric material was removed on a short silica gel column (eluant: dioxane-benzene 1:3). The material which passed

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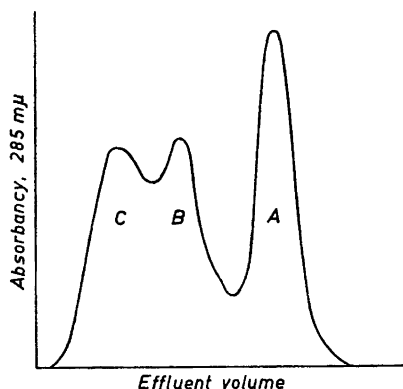


Fig. 1. Gel filtration of acidolysed spruce Björkman lignin (lower-molecular weight fraction of the reaction mixture, see text). Gel material: Sephadex G-25. Eluant: dioxane-water 1:1.

this column, on gel filtration (Sephadex G-25) with dioxane-water 1:1 as eluant, gave the elution diagram shown in Fig. 1.

For further separation the Sephadex filtrate was divided into three fractions corresponding to peaks A, B and C (Fig. 1) and fractions A and B were subjected to silica gel chromatography.

Fraction A, which contained 12 % by weight of the lignin used, was found to be a mixture of monomeric compounds. Silica gel chromatography using gradient elution (benzene-ethyl acetate, with gradually increasing content of the latter solvent) provided the ketol I (6 % of the lignin) and a variety of further monomers (about 4 % of the lignin) including, in addition to the above-mentioned products, vanillic acid, 1-(4-hydroxy-3-methoxyphenyl)-2-propanone and 1-(4-hydroxy-3-methoxyphenyl)-1,2-propanedione. Finally, the hitherto unknown 3-hydroxy-1-(4-hydroxyphenyl)-2-propanone, m.p. 72-73°, was obtained. Structural proof was provided by comparison with a synthetic sample prepared according to a method previously described<sup>3</sup> for the synthesis of ketol I.

Silica gel chromatography of fraction B gave, in addition to a few still unidentified products, 4,4'-dihydroxy-3,3'-dimethoxystilbene as well as a compound, m.p. 110°, which by its UV absorption was characterized as a phenylcoumarone (*cf.* Ref.<sup>4</sup>). On the basis of its IR spectrum and the synthe-