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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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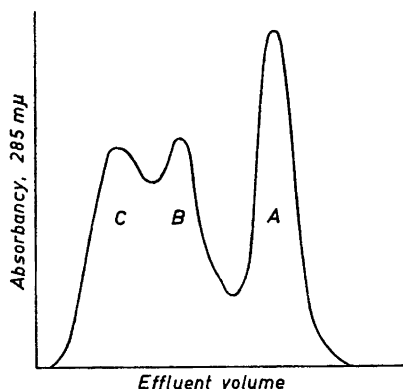


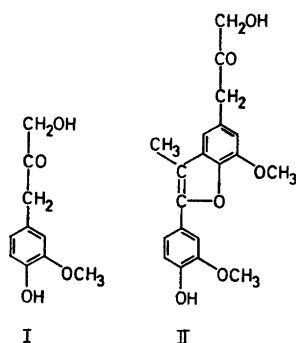
Fig. 1. Gel filtration of acidolysed spruce Björkman lignin (lower-molecular weight fraction of the reaction mixture, see text). Gel material: Sephadex G-25. Eluant: dioxane-water 1:1.

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'-dimethoxy-stilbene 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-



sis<sup>5</sup> of an identical product starting from dehydrodiconiferyl alcohol,<sup>6</sup> the substance is assigned structure II. Further work to confirm this structure is in progress.

From the brown-coloured, probably oligomeric and polymeric acidolysis products which were accumulated in fraction C, no individual products have been isolated so far.

The relation of the degradation products mentioned above to specific lignin structures will be discussed in forthcoming detailed publications.

In gel filtration of aqueous solutions of aromatic compounds, the "molecular sieving" action of the gel (Sephadex) was found<sup>7</sup> to be obscured by adsorption effects. It was therefore surprising to find that fractionation in the order of molecular size had taken place in the experiments reported above.

Gel filtration experiments<sup>8</sup> with mixtures of lignin model compounds (monomeric models such as ketol I, 2-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-1-propanone and vanillin, as well as dimeric models such as pinoresinol and dehydrodiconiferyl alcohol), showed that adsorption effects were greatly suppressed if mixtures of water and certain polar organic solvents (e.g. dioxane) were used as eluants.

It is intended to apply the combination of gel filtration and chromatographic separation methods to lignin degraded in different ways. An investigation of lignin degradation products obtained under the conditions of kraft and soda cooking is presently being carried out.

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## Ozonolysis of Acetylenedicarboxylic Acid

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Ozonolyses in formic acid with the formation of performic acid have been reported.<sup>1,2</sup> Investigations on this reaction have recently been extended to maleic acid and its anhydride.<sup>3,4</sup>

Acetylenedicarboxylic acid, dissolved in concentrated formic acid, did not absorb ozone quantitatively, and a large excess of the reagent had therefore to be applied in order to ensure a complete reaction. The reaction mixture contained active oxygen, but performic acid could not be detected by direct titration nor by distillation *in vacuo*. After evaporation of the solvent, the reaction product was a mixture of crystals. About one fourth of it was oxalic acid and the remainder an acid  $C_2H_4O_6$ . This acid was dibasic and contained one atom of active oxygen. It could be reduced to tartronic acid and dehydrated to mesoxalic acid. The evidence should prove the new acid to be hydroperoxymaleonic acid (I).