A Further Proof of the Identity of Natural and Biosynthetic Lignin

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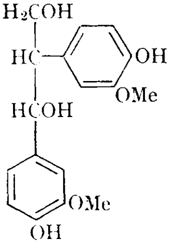
THE detection of aryl benzyl ethers in lignin[1] prompted us to cleave these labile linkages carefully so that no subsequent condensations of the condensation products occur. In this way, minute amounts of those dilignols have been obtained from spruce lignin.[2,3] They form the main intermediates of the preparation of artificial lignin by dehydrogenation of coniferyl alcohol, *viz.*, dehydrodiconiferyl alcohol, pinoresinol, and guaiacylglycerol β-coniferyl ether. Degradation of spruce lignin gave in addition a new cleavage product, the crystalline diguaiacylpropanediol (I).[2,4] Recently two trilignols and even a tetralignol in which the propanediol (I) occurs have been obtained by degradations. In our opinion, since lignin synthesis follows the same course *in vitro* and *in vivo*, (I) ought to occur among the products of dehydrogenation of coniferyl alcohol.

After the properties of (I) had been studied, a substance was detected, among the numerous products which accompany the crude guaiacylglycerol β-coniferyl ether formed on dehydrogenation of coniferyl alcohol, with chromatographic properties which suggested that it was the propanediol (I). Vast losses were however incurred during its isolation.

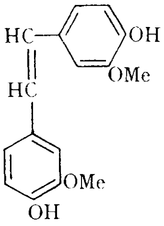
The propanediol (I) has a remarkable characteristic: on heating in aqueous alkali or acid it loses formaldehyde and water forming 4,4′-dihydroxy-3,3′-dimethoxystilbene (II), a stable compound with a charactistic fluorescence. This material was discovered during alkali treatment of spent sulphite liquors from spruce[5] and has since been frequently encountered, most recently as a conversion product from spruce milled-wood lignin.[6] Apart from its fluorescence the stilbene can be readily recognized by its chromatographic behaviour.

It is a central question in lignin chemistry whether lignin is produced in Nature as it is *in vitro* by dehydrogenation of coniferyl alcohol and its congeners. There are strong arguments in favour of this belief. Here we have another opportunity of testing it, since, if this belief is correct, the propanediol (I) should also occur among the dehydrogenation products or be detectable in the form of the stilbene.

This expectation has been fulfilled. Both artificial lignin made from coniferyl alcohol and the fraction of the lignification intermediates suspected to contain (I) were treated with alkali. The stilbene (II) was definitely detected in the resultant reaction mixture by its fluorescence and its behaviour on chromatography in three solvent systems. After methylation, the methyl ether of (II) has also been detected.



(I)



(H)

(*Received, January 26th,* 1966; *Com.* 048.)

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