Observations on Lignin

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LIGNIN has a highly condensed molecular structure, and hence very vigorous reactions must be used to achieve any far-reaching degradation of the material. When lignin is heated with strong alkali, methylated, and oxidised with potassium permanganate, it affords a large number of degradation products, mostly monomeric methoxylated benzenecarboxylic acids.[1] A few methoxylated acids containing two benzene rings are also obtained. A small amount of a new member of the latter category, *viz.* 4,5,5′,6′-tetramethoxybiphenyl-2,3′-dicarboxylic acid (I), has now been isolated[2] (dimethyl ester, m.p. 153—154°*).

The discovery that lignin contains some aryl benzyl ether linkages[3] which are easy to hydrolyse but which also readily undergo condensations incited attempts to secure well-defined oligomeric fractions of the lignin polymolecule by means of extremely mild hydrolysis. Since the reliability of paper chromatography in this field is open to scepticism, it was our aim to secure crystalline samples or derivatives of identifiable degradation products. Finely powdered spruce wood (*Picea excelsa* L.) was freed from soluble phenolic constituents, and subjected to mild hydrolysis with methanol containing 0·5% of hydrogen chloride at 20° for 48 hours; after dilution with water, small amounts of crystalline dehydrodiconiferyl alcohol[4] and (±)-pinoresinol[4] were isolated and characterized.[5] Guaiacylglycerol β-(coniferyl ether)[4] was also obtained from spruce as a crystalline derivative after continuous extraction with 2% acetic acid at 100°.[6] Analogous hydrolysis of pre-extracted beech powder (*Fagus sylvatica*) led to the isolation of (±)-syringaresinol (dimethoxypinoresinol)[6] [previously obtained by dehydrogenation of sinapyl alcohol (4-hydroxy-3,5-dimethoxycinnamic alcohol)[7]], together with α-(4-hydroxy-3,5-dimethoxyphenyl)glycerol* (II)[8] and 1,2-bis-(4-hydroxy-3,5-dimethoxyphenyl)propane-1,3-diol* (III).[8] In addition, coniferyl alcohol[4] and coniferaldehyde were obtained from both spruce and beech, and sinapyl alcohol and sinapaldehyde from beech on hydrolysis with water alone.[8] The yields of identifiable crystalline substances obtained by mild hydrolysis of beechwood constitute up to 10% of its lignin content, but the yields from spruce are much less. The structure of (II) has been confirmed by synthesis.[8] Substance (III) can be readily converted[8] into a known stilbene derivative.[9] The formation of (III) can be conjectured to occur by combination of the mesomeric forms (IV) and (V) of free radicals derived by enzymatic dehydrogenation of sinapyl alcohol in the plant, with simultaneous elimination of the three-carbon side-chain of (V).

When [^{14}CHNH$_2$]-L-phenylalanine[10] or [β-^{14}C] coniferin[11] were infused into fresh shoots of spruce saplings, lignin preparations were later isolated which on oxidative degradation[1] yielded weakly

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* These compounds gave satisfactory analyses.

[1] K. Freudenberg, C.-L. Chen, and G. Cardinale, *Chem. Ber.*, 1962, **95**, 2814.

[2] K. Freudenberg and C.-L. Chen, unpublished results.

[3] K. Freudenberg, J. M. Harkin, and H.-K. Werner, *Chem. Ber.*, 1964, **97**, 909.

[4] For formulæ see K. Freudenberg, *Nature*, 1959, **183**, 1152.

[5] K. Freudenberg and J. M. Harkin, unpublished results.

[6] H. Nimz, *Chem. Ber.*, 1965, **98**, 533, 538.

[7] K. Freudenberg, J. M. Harkin, M. Reichert, and T. Fukuzumi, *Chem. Ber.*, 1958, **91**, 581; K. Weinges, *ibid.*, 1961, **94**, 2522.

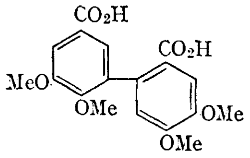
[8] K. Freudenberg and H. Nimz, unpublished results.

[9] H. Richtzenhain, *Ber.*, 1944, **77**, 409; I. A. Pearl, *J. Org. Chem.*, 1957, **22**, 1229.

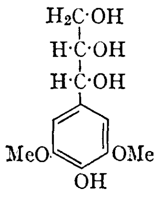
[10] K. Freudenberg and B. Lehmann, *Chem. Ber.*, 1963, **96**, 1850.

[11] K. Freudenberg and H. Renner, unpublished results.

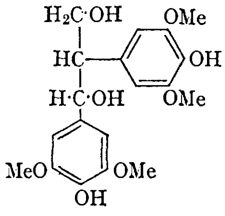
radioactive veratric acid[10,11] and dehydrodiveratric acid.[11] A dehydrogenation polymer (DHP) made from [β-^{14}C]coniferyl alcohol, *i.e.* an artificial, biosynthetic lignin,[12] also gave weakly radioactive veratric acid.[11] The formation of moieties in spruce [β-^{14}C]lignin which can give rise to radioactive veratric acid can be explained by the participation of free radicals of the coniferyl series analogous to (IV) and (V) during the growth of the lignin polymolecule. A minute amount of the guaiacyl analogue of (III) has been isolated from spruce lignin.[8]



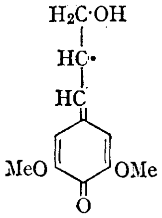
(I)



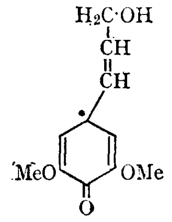
(II)



(III)



(IV)



(V)

Radioactive lignin extracted from spruce saplings which had sucked up a solution of [β-^{14}C]-coniferin gave isohemipinic and metahemipinic acids with specific radioactivities of 53% and 12%, respectively, relative to the activity of the lignin. Artificial lignin (DHP) made from [β-^{14}C]coniferyl alcohol gave the same acids with specific activities of 49—52%[12] and 10·5%[11] compared with the activity of the original DHP. This is a convincing demonstration of the resemblance between natural and artificial lignin.

Formulae (IV) and (V) represent two of the four possible mesomeric forms of the free radicals produced by phenol dehydrogenation of sinapyl alcohol. The corresponding mesomeric free radicals produced by dehydrogenation of coniferyl alcohol with peroxidase–hydrogen peroxide have now been detected by e.s.r. spectroscopy,[5] albeit in 50% aqueous dioxan at 20° and not in aqueous solution, the conditions used for producing biosynthetic lignins *in vitro*.[12] The decay of the e.s.r. signal indicated a half-life of the mesomeric free radicals of 45 seconds.

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[12] K. Freudenberg, K. Jones, and H. Renner, *Chem. Ber.*, 1963, **96**, 1844.