Estimation of "Uncondensed" Phenolic Units in Spruce Lignin

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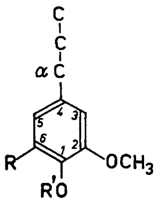
Previous work by Freudenberg and several other authors (for literature, see Ref.[1]) has established the presence of two general types of arylpropane units in conifer lignin. One of them is characterised by an unsubstituted 6-position ("uncondensed" units, I and Ia, with free and etherified phenolic hydroxyl group, respectively). In the other type ("condensed" units, II and IIa) the 6-position is substituted by a carbon atom, either of an aromatic ring (diphenyl structure) or of the side-chain of an adjacent arylpropane unit. The coumaran system, in which R and R′ are two carbon atoms of the hydrofuran ring, is an important representative of type IIa.

Various attempts have been made to estimate the relative amounts of these two types of units in lignin. From the yields of vanillin obtained on nitrobenzene oxidation, Leopold [2] concluded that lignin contains about equal amounts of both types. Mikawa and co-workers [3], studying the Mannich reaction of a thiolignin, reached the conclusion that 25—40 % of the phenolic nuclei (I and II) of this material were "uncondensed" (I).

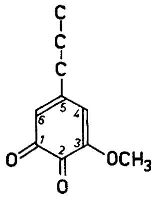
We wish to report that the number of "uncondensed" units with a free phenolic hydroxyl group (I) can be estimated by means of an oxidation with potassium nitrosodisulphonate, ON(SO$_3$K)$_2$ (Fremy's salt). Teuber and Staiger [4] have shown that this reagent yields *o*-benzoquinones when acting on 4-substituted guaiacol compounds. In extension of this work, a variety of lignin model compounds of type I has now been found to be readily converted into the exceptionally stable 3-methoxy-1,2-benzoquinones (III). For instance, quinone IV (m.p. 69—70°) was obtained from ethylguaiacylcarbinol methyl ether. Similarly, dihydro-dehydrodi*iso*eugenol gave an *o*-quinone of m.p. 98—99°, and (+)-pinoresinol yielded the expected bis-*o*-quinone (decomp. >170°, phenazine derivative, decomp. >200°). Guaiacol compounds which were substituted in both the 4- and 6-positions, *i.e.*, models for the "condensed" type II, were not appreciably attacked by Fremy's salt.

The above-mentioned model *o*-quinones of type III, dissolved in glycol monomethyl ether-water (3 : 2), had very similar absorption curves with a main maximum at 365—367 mμ and a broad maximum or shoulder at about 465 mμ (*cf.* Ref.[5]); the $\varepsilon_{\max}$ values, based on one phenolic guaiacyl equivalent of the starting material, were 2 500 and 700—800, respectively. Spectrophotometric examination of the reaction between the phenols and Fremy's salt indicated a 90 % yield of the *o*-quinones.

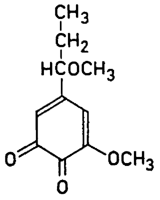
For the application of Teuber's reaction to lignin, the following two exceptions were important. Firstly, guaiacol compounds of type I, which carried a keto



I. R = R′ = H
Ia. R = H; R′ = C
II. R = C; R′ = H
IIa. R = C; R′ = C

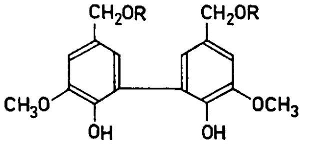


III



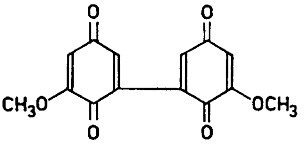
IV

group in the α-position (*e.g.*, 4-propioguaiacone), did not react with Fremy's salt, the 6-position being deactivated by the 4-carbonyl substituent. Secondly, when treated with Fremy's salt, guaiacylcarbinols (type I, the α-C carrying H and OH) suffered *p*-oxidative cleavage rather than the normal *o*-oxidation. For instance, guaiacylethylcarbinol gave methoxy-*p*-quinone and propionic aldehyde. (As mentioned above, the corresponding carbinol methyl ether reacted in the normal way, yielding the *o*-quinone IV.) Similarly, dehydrodivanillyl acohol (V[6]) was oxidised to the di-*p*-quinone VII, m.p. 200°. The methyl ether VI, formed from V in methanolic hydrochloric acid (20°), was not attacked by Fremy's salt.



V. R=H

VI. R=CH_3



VII

The findings just mentioned made it necessary to remove the minor amounts of α-keto and α-carbinol groups present in the phenolic units of lignin. Björkman lignin was therefore reduced with sodium borohydride and subsequently treated with a solution of 0.15 N HCl in methanol-dioxan 1 : 1 (20°, 48 h); these operations converted the α-groupings mentioned into $>CH(OCH_3)$ groupings [7].

Oxidation of this pretreated lignin in glycol monomethyl ether-water with Fremy's salt produced a red solution, the absorption spectrum of which was very similar to that of the model *o*-quinones in the same solvent. Comparison of the ε-values of the oxidised lignin solution in the range above 360 $m\mu$ with those of the solutions of the similarly produced model *o*-quinones indicated the presence of 0.15 – 0.18 "uncondensed" phenolic units (I) per methoxyl group of the lignin. Since Björkman lignin contains about 0.30 phenolic hydroxyl groups per OCH_3, the result obtained means that, of the total of phenolic guaiacylpropane units (I + II), 50 – 60 % are of the "uncondensed" type (I) and 40 – 50 %, *i.e.* 0.12 – 0.15 units per OCH_3, of the "condensed" type (II).

The results reported here give no information regarding the ratio between "uncondensed" and "condensed" units of the non-phenolic type (Ia and IIa). As shown before [8], lignin contains about 0.08 coumaran units per OCH_3; thus, "condensed" units of this type would make up about 12 % of the non-phenolic portion of the lignin molecule. The distribution of the remaining types of "condensed" units, especially the diphenyl elements, will be discussed in a forthcoming detailed publication.

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