The Occurrence of Non-cyclic Benzyl Ether Bonds in Lignin

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Summary. The structure of the non-cyclic benzyl aryl (α-0-4) ethers 4 and 5, proposed by Freudenberg and Friedmann (1960) and recently doubted by Leary (1980), is discussed on the basis of previously published experimental results. Further evidence in favor of the occurrence of non-cyclic α-0-4 bonds in lignin is provided. A critical comment is, however, given on the formation of non-cyclic α-0-γ bonds in lignin according to Leary (1980).

Non-cyclic Benzyl Aryl Ether (α-0-4) Bonds in Lignin

The occurrence of non-cyclic benzyl aryl ether (α-0-4) bonds in lignin was proposed by Freudenberg and Friedmann (1960) when they identified two α, β-diaryl ethers, trilignol 4 and tetralignol 5, among the products obtained by dehydrogenative polymerization of coniferyl alcohol (2). The authors assumed that these non-cyclic α-0-4 lignols 4 and 5 are formed by the addition of either coniferyl alcohol (2) or dehydro-diconiferyl alcohol (3) onto the intermediate quinone methide 1. The existence of such ether bonds in spruce lignin was later confirmed by Freudenberg et al. (1964) as well as by Adler et al. (1966).

Recently in this journal, Leary (1980) has claimed that “proof of the structures of lignols 4 and 5 was ambiguous, being based on hydrolysis of the benzyl ether bonds of the two lignols to give the known compounds coniferyl alcohol (2), dehydro-diconiferyl alcohol (3) and guaiacylglycerol-β-coniferyl ether.” He instead suggested that the “products isolated by Freudenberg and coworkers were formed by addition of the terminal aliphatic, not the phenolic, hydroxyl groups”, and should have structures 4’ and 5’, respectively. Leary further mentions that “knowledge of the nature of the benzyl ether linkage in compounds 4 and 5 is critically important in understanding the molecular structure of lignins”, and that “a re-examination of the structures of lignols 4 and 5 would clarify our understanding of lignin structure and biosynthesis.”

I would like to point out that Freudenberg and Friedmann (1960) in their paper, cited by Leary, clearly explained that the main evidence for structures 4 and 5 was based on the analyses of the dinitrophenyl ethers, obtained from lignols 4 and 5 by the reaction with dinitro-fluorobenzene, which is known (Zahn and Wuerz 1951) to etherify
Scheme 1.

Scheme 2.