A New Class of Linkage Between Carbohydrates and Lignin Model Compounds

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Summary Aqueous solutions of glucose and vanillyl alcohol react under mild conditions to form an ether linkage between the benzyl and glucose C-6 positions; this strongly suggests the possibility of a similar bond between lignin and cellulose.

The difficulty in separating lignin from carbohydrates has been attributed to the presence of lignin–carbohydrate bonds, but the nature of such bonds has been the subject of much speculation.[1] Freudenberg[2a] has suggested that bonds are formed by the addition of carbohydrates to quinone methides. The major drawback to this proposal is that in the plant, carbohydrates would have to compete with water. An alternative method of forming bonds would be through the etherification of benzyl alcohol residues (occurring on 15% of units in spruce lignin[2b]) with carbohydrates. Such etherification occurs when *p*-hydroxybenzyl alcohols are heated in alcohols, or react in acidic media.[4,5]

We have found that this reaction occurs under quite mild conditions in aqueous media. Thus warming (60 °C) a solution of vanillyl alcohol (1 g) in aqueous acetate buffers (90 ml, 0·05M) containing ethanol (10 ml) gives the aliphatic ethyl ether of vanillyl alcohol (32% after 8 days, pH 4; 33% after 28 days, pH 5). The ethyl ether was also formed at room temperature over the pH range 4—8. (Yields are not available as final equilibrium could not be guaranteed.) Thus, given sufficient time under mild conditions a dilute solution of alcohol can lead to a significant amount of etherification. In view of the relative abundance of *p*-hydroxybenzyl alcohol groups in lignin, and the concentrations of carbohydrate, a lignin carbohydrate bond could be formed in this way.

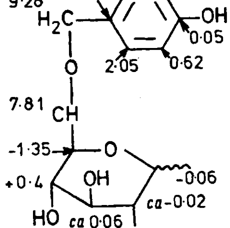

Figure. Proposed structure for glucose–vanillyl alcohol adduct, together with relevant ^{13}C n.m.r. data. The figures shown are δ(adduct) − δ(starting material) p.p.m.

We have demonstrated that this reaction occurs for glucose. Thus warming (60 °C) vanillyl alcohol (1 g) in an aqueous acetate buffer (100 ml, 0·05M) containing glucose (40 g) produces an anomeric mixture of two glucose vanillyl alcohol derivatives (48% yield, 10 days, pH 4). The existence of the linkage was verified by elemental analysis and by the mass spectrum of the per-acetylated derivative (M^+, 526). This was supported by the ^{1}H n.m.r. spectrum, which also indicated the anomeric mixture (50:50).

The site of the linkage was shown by ^{13}C n.m.r. spectroscopy to be between the benzyl carbon and the glucose C-6. The proposed structure is shown in the Figure, and the values for the chemical shift changes show clearly that the bonding is through the glucose C-6. (The shifts for each glucose anomer were obtained from literature figures,[5] and for vanillyl alcohol from an authentic sample. As the changes in chemical shift between adduct and glucose were almost identical for each anomer, the differences have been averaged.)

No other vanillyl alcohol–glucose adducts could be detected, and this clearly indicates that there is a marked preference for the participation of the primary hydroxy-group in this etherification. As primary hydroxy-groups should be available in both cellulose and hemicellulose, and in view of our results, we should expect these to be involved to some extent in bonding to lignin.

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[1] K. V. Sarkanen and Y. Z. Lai in 'Lignins,' eds. K. V. Sarkenen and C. H. Ludwig, Wiley-Interscience, New York, **1971**, p. 218.

[2] K. Freudenberg in 'Constitution and Biosynthesis of Lignin,' eds. K. Freudenberg and A. C. Neish, Springer-Verlag, New York, 1968, (a) p. 93, (b) p. 107.

[3] J. De Jonge and B. H. Bibo, *Recrueil*, 1966, **74**, 1448.

[4] B. Leopold, *Svensk. Papperstidn.*, 1952, **55**, 816; S. Larsson and B. Lindberg, *Acta Chem. Scand.*, 1962, **16**, 1757.

[5] P. Colson, K. N. Slessor, H. J. Jennings, and I. C. P. Smith, *Canad. J. Chem.*, 1975, **53**, 1030.