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Solution and Solid State ^{13}C-NMR of Barley Straw Lignins

L. A. RAMSEY, A. PATERSON, AND P. M. A. BRODA

Department of Biochemistry and Applied Molecular Biology, UMIST, Sackville Street, Manchester M60 1QD, UK

AND

J. D. POWNALL AND I. J. F. POPLETT

BP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN, UK

ABSTRACT

Grass lignins are formed by the polymerization of phenoxy radicals and contain a variety of carbon–carbon and carbon–oxygen bonds. They are similar to the hardwood lignins, but differ by containing a substantial proportion of esterified cinnamic acids.

Detailed nuclear magnetic resonance studies in conjunction with chemical analysis have given new information on the structure of grass lignins.

Milled straw lignins (MSL) from barley were examined by both solution and solid-state (CP/MAS) NMR before and after acetylation. The assignment of the carbon-13 (100 MHz) solution spectra was achieved using model compound data, nuclear Overhauser enhancement (NOE) suppression, and insensitive nuclei enhanced by polarization transfer (INEPT) techniques. The NOE suppression permitted quantitative analysis of lignin, giving information on the ratio of specific carbon atoms. Use of the relaxation agent, chromium acetylacetonate, enabled accumulation of sufficient spectral data to give a spectrum suitable for integration after 90 h.

The INEPT technique, which had not previously been used for lignin analysis, was successfully applied to acetylated MSL. This technique increased signal intensities 3–4-fold and simplified the spectrum by inverting methylene carbons and eliminating or inverting quaternary carbons. Comparison of this spectrum with the normal spectrum permitted accurate assignment of quaternary and methine carbons.

The solid-state carbon-13 CP/MAS NMR was used to examine *in situ* lignin and the isolated MSL. The ^{13}C-CP/MAS spectrum of *in situ* lignin shows that

cellulose and hemicellulose resonances dominate with little evidence of the aromatic structure of lignin. the ^{13}C-CP/MAS of MSL shows reduced carbohydrate resonances and increased aromatic resonances. The extent of modification to the barley straw was estimated and results indicate the presence of lignin–carbohydrate complexes.

Detailed information on the nature of the linkages between lignin components and between lignin and carbohydrate components has been obtained from these spectra.