^{13}C NMR Studies on a New Method for Lignin Characterization

F. Lu and J. Ralph

Introduction

Despite great progress in lignin chemistry, precise elucidation of lignin structure is still a challenge for chemists. Recently we developed a simple and powerful method which selectively and efficiently cleaves α-ether and β-ether linkages to allow quantitative analysis of lignin structural units involved in uncondensed structures (see preceding paper). In this paper we report our investigation using NMR techniques to show the high selectivity, high yield conversions involved in the method.

Experimental

The analysis procedure is described in the preceding summary. ^{13}C NMR spectra of lignin models and lignin derivatives in acetone-d_6 were recorded under standard small-molecule conditions on a Bruker AMX-360 instrument; the central solvent peaks were used as internal reference (^{1}H, 2.04 ppm; ^{13}C, 29.80 ppm).

Discussion

Our method includes three key steps: bromination, two-electron reductive cleavage, and hydrogenation. The ^{13}C NMR spectra of acetyl bromide treated model compounds (**A** and **C**) and milled wood lignins (**B** and **D**) are shown in Fig. 1. β-Aryl ether models are quantitatively converted to acetylated α-bromides as shown in Fig. 1 (**A**, **C**) and β-aryl ether substructures in lignins are also converted to the corresponding derivatives which have the same characteristic peaks (C_α, C_β and C_γ are shown in Fig. 1). It is also seen that the major linkage between kenaf (**C**) lignin units is the γ-O-4 aryl ether which forms linear lignin chains; therefore, it is expected that the amount of monomers, released by β-aryl ether cleavage, from pine lignin will be lower than from kenaf lignin (see preceding paper). Fig. 2 clearly shows that the final degraded products by this method are those

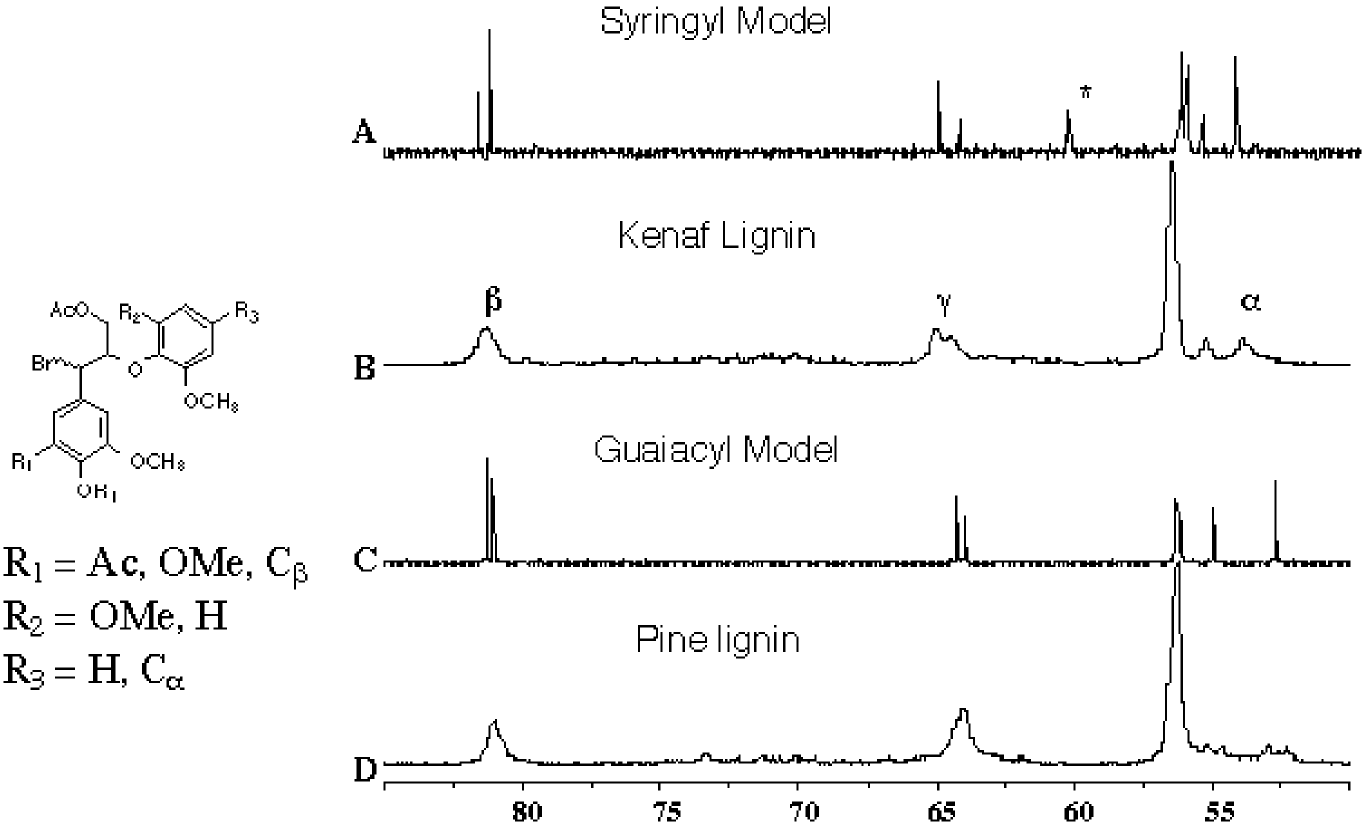

Figure 1. Sidechain region of ^{13}C NMR spectra of AcBr treated lignin models and lignins: A, syringyl model; B, kenaf lignin (an S-rich S/G lignin); C, guaiacyl model; D, pine lignin (a G-lignin).

from lignin structural units linked through β-aryl ethers. In other words, the degraded monomer of pine lignin is 3-(4-acetoxy-3-methoxy)phenylpropyl acetate from guaiacyl units linked by β-aryl ethers. Monomers from kenaf lignin are the same product from guaiacyl components as well as 3-(4-acetoxy-3,5-dimethoxy)phenylpropyl acetate from syringyl units connected by β-aryl ethers.

The new method for characterization of lignin provides us with the ability to look at both steps by NMR. After AcBr treatment, α-ethers are broken and the lignin has been derivatized but is otherwise intact (Fig. 1). Following β-ether cleavage in the two-electron reductive step, the lignin becomes extensively degraded. The material extracted into ether is primarily monomers with small amounts of higher oligomers.

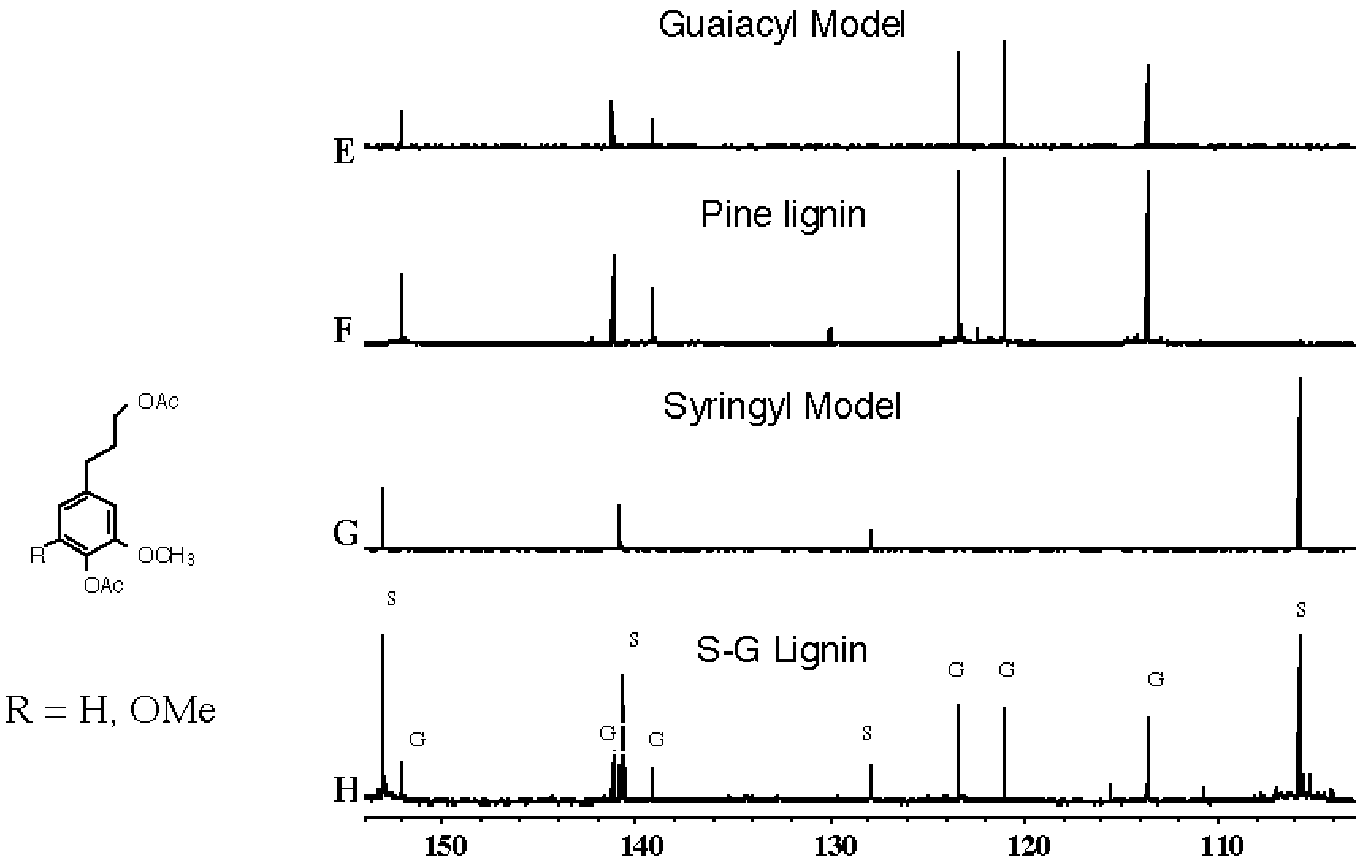

Figure 2. Sidechain region of ^{13}C NMR spectra of models and degradation products (mainly monomers) for lignins: E, guaiacyl model; F, pine lignin; G, syringyl model; H, an S/G lignin.