Preparation and Value of Synthetic Lignins with NMR-Invisible Methoxyl Groups

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Introduction

NMR spectroscopy is an invaluable aid to determining details of the structures of cell wall components including lignin. And synthetic lignins, so-called DHPs, are enormously valuable to elucidate reaction pathways and provide the NMR data required to interpret spectra from real plant materials. One problem with lignin and DHP spectra is systematic artifacts that arise from various machine imperfections, vibrations of many types, and our impatience for the spectra which dictates that we run acquisitions before the poor nuclei have 'relaxed' properly. The most troubling problem is an artifact known as T_1-noise, a particular problem around the intense methoxyl peaks (in both proton and carbon dimensions of 2D spectra), where artifacts obliterate or obfuscate the data in that region. In this report, we illustrate a method to synthesize the coniferyl alcohol with an isotopically modified methoxyl group and transfer it into a DHP. This provides a rather slick method for rendering methoxyls in synthetic lignins NMR-invisible, greatly improving the appearance and interpretability of NMR spectra.

Methods

Coniferyl alcohol with NMR-invisible methoxyl group was synthesized as shown in Fig. 1. It was biomimetically converted into DHPs by established methods. 2D NMR methods were essentially standard Bruker versions.

Results and Discussion

An elegant solution to the methoxyl region T_1-noise artifact problem is possible for synthetic lignins; for real lignins, this is not possible but, as noted in an accompanying report, there is also an instrumental solution. The idea for synthetic lignins is to make the methoxyl group NMR-invisible, but normal in every other regard. That can be done by replacing the normal methoxyl carbon (which has *ca* 1% natural abundance of the NMR-active ^{13}C) by the ^{12}C isotope (^{13}C-depleted) which is not NMR-active. Replacing the protons with deuterons also removes the methoxyl from the proton spectrum.

As shown in Fig. 2, a variety of 2D NMR spectra of a DHP produced from the specialized coniferyl alcohol **7** are spectacularly superior to an equivalent DHP made from normal coniferyl alcohol. The spectra also illustrate the value of spectral editing in 2D NMR experiments that has not yet attracted much attention from lignin chemists. The DEPT-HMQC experiment can aid in assignment by selectively inverting (for example) $-CH_2$ resonances (Fig. 2C).

The freedom from artifacts in these spectra will allow more detailed assignments to be made and aid in the characterization of real plant lignins.

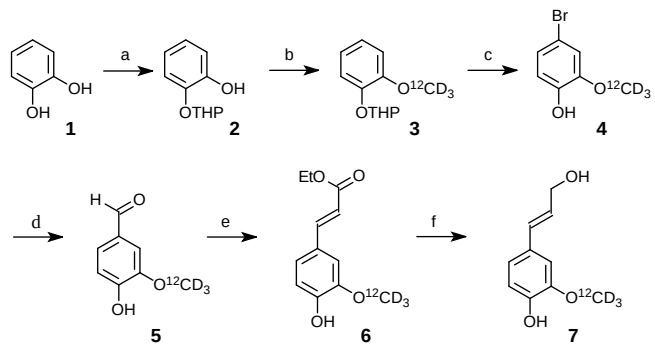

Figure 1. Synthetic scheme to produce coniferyl alcohol with an NMR-invisible methoxyl group.

Figure 2. Over page.

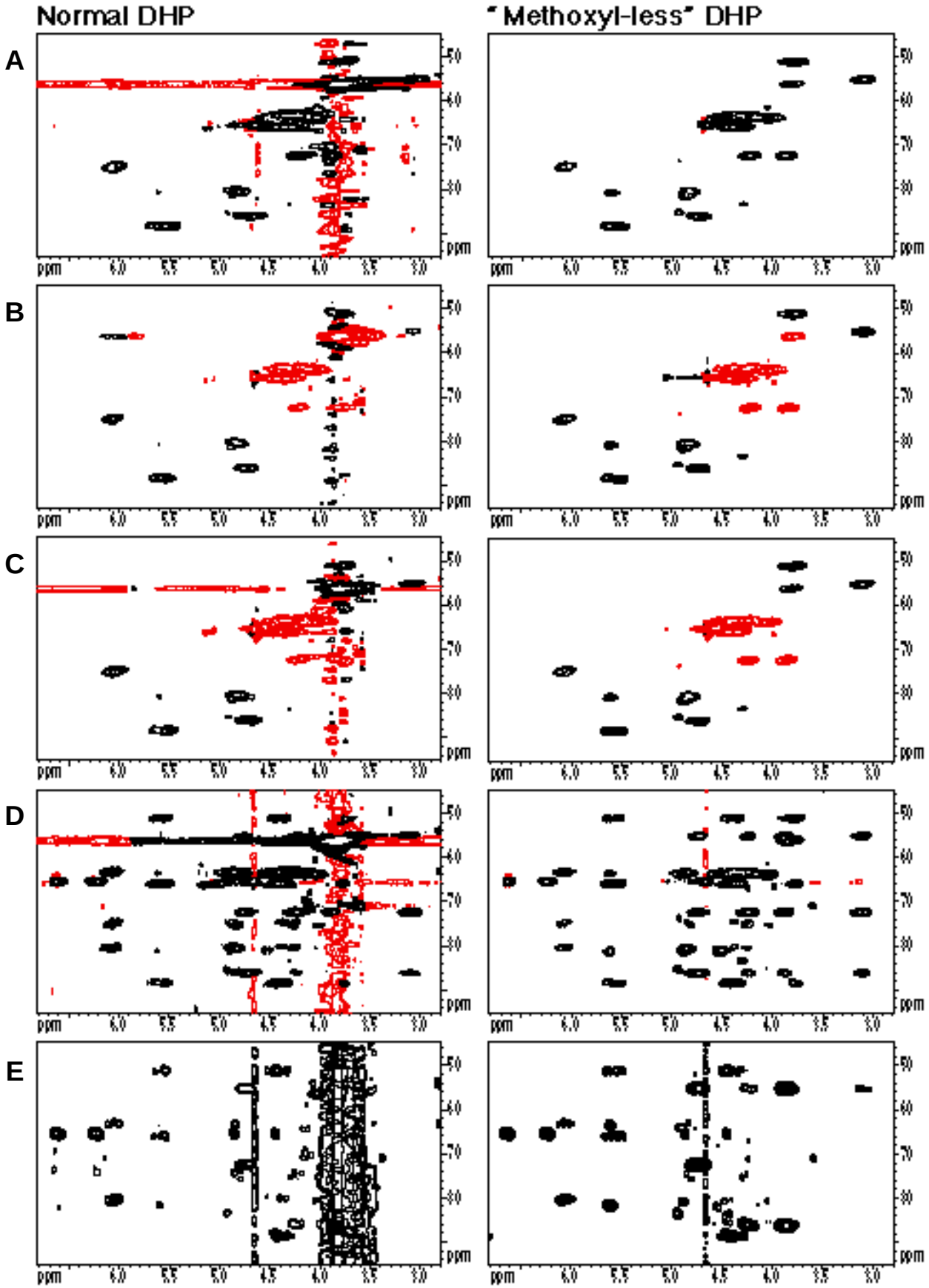

Figure 2. 2D NMR spectra of synthetic DHPs made using (left) normal coniferyl alcohol and (right) 'methoxyl-less' coniferyl alcohol. A) HMQC, B) DEPT-HMQC with a $\pi/3$ editing pulse (CH's up, CH_3's and CH_2's down), C) DEPT-HMQC with a π editing pulse (CH's and CH_3's up, CH_2's down), D) HMQC-TOCSY, E) HMBC. Red peaks are negative.