

NMR of Lignin Model Quinone Methides. Corrected ^{13}C NMR Assignments via C-H Correlation Experiments

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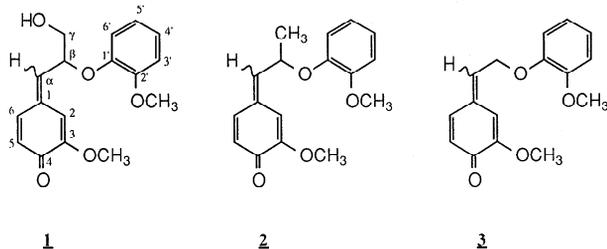
Corrected ^{13}C NMR Assignments via C-H Correlation Experiments

Summary

Carbon-Proton correlation experiments, *via* one-bond and long-range couplings, have allowed complete and unambiguous assignments of all ^{13}C resonances for both the *syn* and *anti* isomers of three lignin model quinone methides.

Introduction

Quinone methides have been well established as important reactive intermediates in the alkaline reactions of wood lignin under pulping conditions (Gierer 1970). Owing to the complexity of the lignin polymer, fundamental studies often rely on the use of appropriate low molecular weight model compounds. Quinone methides **1**–**3** have been used extensively to model the so-called β -aryl ether quinone methide structure generated in lignin.



Several years ago we reported an improved method for the preparation of quinone methides (Ralph and Young 1983). Lignin model quinone methides prepared in this way were relatively stable in solution,

and suitable for NMR investigations (Ralph and Adams 1983). We were able to report the first proton NMR spectra of a range of lignin model quinone methides and showed that guaiacyl quinone methides such as **1**–**3** were formed as mixtures of approximately 70:30 *syn:anti* isomers (Ralph and Adams 1983). The sole ^{13}C NMR spectrum (of **1**) obtained was assigned (incorrectly, Ede 1987) on the basis of available lignin model data, aided by correlation tables.

The recent development of a multitude of useful NMR pulse experiments has now allowed us to make a complete and unequivocal assignment of all carbon resonances in each isomer of **1**–**3**. These corrected data have recently become important for the correlation of ^{13}C NMR chemical shifts with electron densities determined from molecular orbital calculations (Elder *et al.* 1988).

Results and Discussion

Quinone methides **1**–**3** were prepared in CDCl_3 by treatment of the corresponding benzyl alcohols with bromotrimethylsilane followed by saturated aqueous sodium bicarbonate, as described previously (Ralph and Young 1983).

Proton NMR data have been published previously (Ralph and Adams 1983). The assignments were aided by deuterium labelling and NOE studies, and were unambiguous.

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Table 1. ^{13}C NMR Shifts of Quinone Methides

	α	β	γ	OCH_3	1	2	3	4	5	6	1'	2'	3'	4'	5'	6'
syn-1	141.1	79.7	64.7	55.8,55.3	134.0	104.0	153.3	181.1	128.4	141.3	146.7	150.7	112.3	123.9	121.3	118.9
anti-1	141.1	79.4	65.1	55.8,55.2	133.8	111.6	152.6	181.3	129.7	132.6	146.5	150.8	112.3	124.0	121.3	119.2
syn-2	146.5	74.4	21.2	55.8,55.1	132.0	104.1	153.1	181.0	128.5	141.6	146.9	151.1	112.3	122.9	120.8	117.7
anti-2	146.4	74.2	21.8	55.8,55.1	131.8	111.9	152.8	181.2	129.7	132.5	146.9	151.1	112.3	122.9	120.8	117.9
syn-3	140.5	66.0	–	55.8,55.3	133.0	104.3	153.1	181.1	128.1	141.4	147.3	149.7	112.0	122.4	120.8	114.1
anti-3	140.1	65.6	–	55.8,55.2	133.0	111.7	152.5	181.4	129.4	132.6	147.3	149.7	112.0	122.4	120.8	114.4

In this study, DEPT experiments (Doddrell *et al.* 1982) rapidly established the multiplicity of all carbons for each quinone methide. The excellent dispersion of proton chemical shifts, particularly in the A-ring, allowed complete assignment of ring A carbons by the C–H correlation experiment (Bax and Morris 1981) or its proton-decoupled analogue (Bax 1983). C–H correlation experiments with delays set for long-range coupling interactions (Reynolds 1984), on the quinone methides and on the parent models allowed complete assignment of ring B carbons also. In the parent model compounds there has long been confusion over the assignment of the oxygenated aromatic carbons (Ralph 1988) but, in both the models and the quinone methides, those bearing methoxyls were readily identified by the long range experiment through the 3-bond interaction between the methoxyl protons and the aromatic carbon (C3 and C2'). Table 1 lists complete assignments.

Experimental

Quinone methides **1–3** were prepared as described previously (Ralph and Young 1983).

All NMR spectra were run at ambient probe temperature in CDCl_3 on a Bruker AC–200 FT spectrometer operating at 200.13 MHz ^1H (50.33 MHz ^{13}C) using either a 5 mm carbon-proton dual probe or a 10 mm multinuclear probe. WALTZ-16 decoupling (Shaka *et al.* 1983) was used for all ^{13}C and 2D experiments. 2D parameters were essentially those used in the previous paper (Ralph 1988).

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