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### Determination of the Conformation and Isomeric Composition of Lignin Model Quinone Methides By NMR

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DETERMINATION OF THE CONFORMATION AND ISOMERIC COMPOSITION OF  
LIGNIN MODEL QUINONE METHIDES BY NMR

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ABSTRACT

Proton and  $^{13}\text{C}$  NMR of representative guaiacyl and syringyl 5-aryl ether quinone methides have shown that guaiacyl quinone methides, generated from the corresponding benzyl bromides, exist as isomeric pairs in approximately a 70:30 ratio, the major isomer having the 3-methoxyl group syn with respect to the side chain. The ring protons at the 2- and 6-positions in the syn- and the anti-isomers respectively are markedly deshielded by steric compression effects; concomitant shielding of these ring carbons is observed in the C-13 NMR. Nuclear Overhauser enhancement experiments define the major solution conformation of these species, the conformation being consistent with the observed predominance of threo-products resulting from nucleophilic addition reactions.

INTRODUCTION

Reactive quinone methide intermediates, formed in base from phenolic lignin subunits possessing an  $\alpha$ -leaving group play an important role in all alkaline pulping schemes. Basic studies

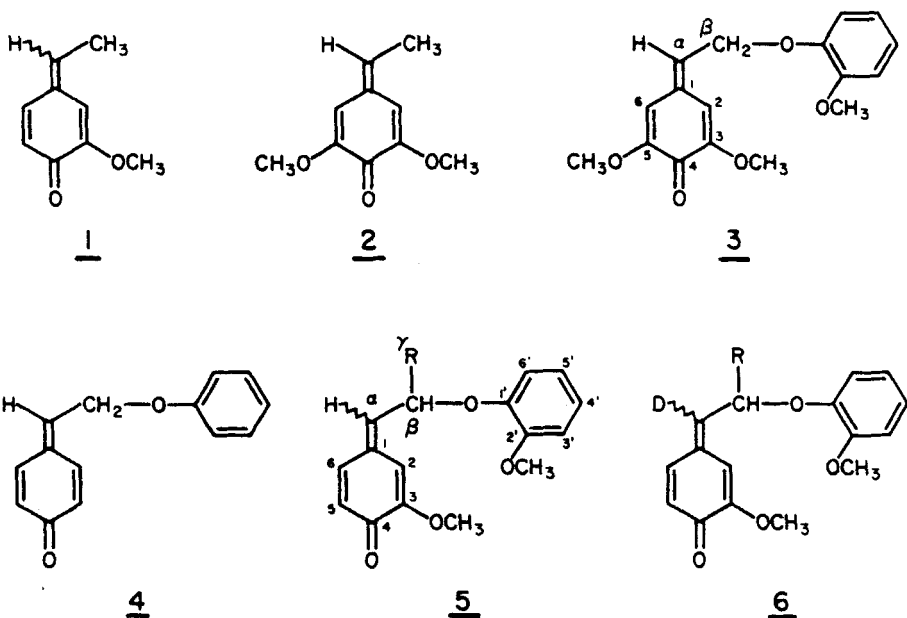
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generally involve the use of appropriate model compounds. A high degree of stereoselectivity for threo-adducts is observed in addition reactions between  $\beta$ -aryl ether lignin model quinone methides and anthrahydroquinone,<sup>1-3</sup> anthranol,<sup>1-3</sup> and amines.<sup>3,4</sup> A critical examination of the conformations of these reactive species in solution is now needed. While much can be inferred from product analysis and examination of molecular models, a study of the intermediates themselves by high resolution NMR was conducted to provide a more complete structural picture.

### RESULTS AND DISCUSSION

Quinone methides 1-6 were prepared in  $\text{CDCl}_3$  by treatment of the corresponding benzyl alcohols with bromotrimethylsilane followed by saturated aqueous sodium bicarbonate as described previously.<sup>4</sup>



a. R = H

b. R =  $\text{CH}_3$

c. R =  $\text{CH}_2\text{OH}$

d. R =  $\text{CD}_2\text{OH}$

Because some of these quinone methides are unstable at room temperature, all were stored in dry ice/acetone until needed. The least stable compounds were 5a and 6a which began to polymerize within 30 min at room temperature; however, solutions of 5b and 6b degassed by the freeze-thaw method<sup>5</sup> could be kept at room temperature for over a week in a sealed tube.

The <sup>1</sup>H NMR spectra (Table 1, Fig. 1) of the monomethoxylated quinone methides 1, 5 and 6 revealed that the products consisted of mixtures of 70% syn- and 30% anti-isomers (Fig. 2). The preference for one isomer over the other is presumably electronic rather than steric in origin since it is the syn-isomer (Fig. 2) which predominates. The isomers were assigned on the basis of the deshielding of H-2 in the syn-form (relative to H-2 in the anti-form) and H-6 in the anti-form (relative to H-6 in the syn-isomer) due to steric compression<sup>6</sup> by the  $\beta$ -carbon substituents. This effect is associated with protons forced to occupy a sterically crowded environment<sup>7</sup> and has been noted repeatedly<sup>8-10</sup> for related structures. In syn-5a (Fig. 3), for example, the Van der Waals volumes of the  $\beta$ -protons overlap with that of H-2. Bond lengths for Fig. 3 were determined from Huckel molecular orbital calculations.<sup>3</sup> In fact the spheres may overlap more extensively than calculated here since the H<sub>2</sub>-H <sub>$\beta$</sub>  distance (1.53 Å), and the calculated angle between the C<sub>2</sub>-H<sub>2</sub> bond and the H<sub>2</sub>-H <sub>$\beta$</sub>  line (64.4°) yield a predicted shielding of only 0.18  $\delta$  from Cheney's equation,<sup>7</sup> compared with the observed 0.35  $\delta$ .

Furthermore, steric compression on H-2(syn) and H-6(anti) induces an electron shift from these protons onto the corresponding carbon atoms, C-2(syn) and C-6(anti), resulting in a shielding effect as illustrated in Fig. 4 for 5c. The factor of approximately 27-fold between the <sup>13</sup>C and <sup>1</sup>H shielding differences (in ppm) for the 2-carbon and 2-proton respectively, is reasonably close to the 20-fold factor indicated by the relative dependence of these shieldings on electron density.<sup>11,12</sup>

TABLE 1

270 MHz <sup>1</sup>H NMR of Quinone Methides in CDCl<sub>3</sub>

QM	Isomer	Methoxyls		2	3	4	5	6	J <sub>5,6</sub>	J <sub>7,6</sub>	Aromatics	a	b	γ	J <sub>ab</sub>	J <sub>BY</sub>	J <sub>Y<sub>1</sub>Y<sub>2</sub></sub>	J <sub>6a</sub>	J <sub>5a</sub>	J <sub>2a</sub>	OH	
		Δ	B																			
1	syn	3.84	-	6.59 <sup>d</sup>	6.42 <sup>d</sup>	7.06 <sup>dd</sup>	9.6	2.2	-	6.49 <sup>d</sup>	2.07 <sup>d</sup>	-	-	-	7.4	-	-	-	-	-	-	-
	anti	3.78	-	6.29 <sup>d</sup>	6.51 <sup>d</sup>	7.54 <sup>dd</sup>	9.9	2.2	-	6.48 <sup>d</sup>	-	-	-	-	-	-	-	-	-	-	-	-
2 <sup>†</sup>	-	3.78, 3.84	-	6.61 <sup>d</sup>	-	6.27 <sup>d</sup>	-	1.8	-	6.38 <sup>d</sup>	2.15 <sup>d</sup>	-	-	-	7.5	-	-	-	-	<.5	-	-
	-	3.79, 3.83	3.89	6.63 <sup>d</sup>	-	6.25 <sup>d</sup>	-	1.8	6.20-7.05 <sup>m</sup>	6.41 <sup>h</sup>	5.06 <sup>d</sup>	-	-	-	6.6	-	-	-	-	<.5	-	-
3 <sup>†</sup>	-	-	-	7.54 <sup>ddd</sup>	6.42 <sup>bdd</sup>	7.14 <sup>dd</sup>	9.9	2.2	6.80-7.35 <sup>m</sup>	6.65 <sup>bc</sup>	5.02 <sup>d</sup>	-	-	-	6.3	-	-	-	-	1.7	-	-
	-	-	-	7.54 <sup>ddd</sup>	6.42 <sup>bdd</sup>	7.14 <sup>dd</sup>	9.9	2.2	6.80-7.35 <sup>m</sup>	6.65 <sup>bc</sup>	5.02 <sup>d</sup>	-	-	-	6.3	-	-	-	-	1.7	-	-
5a	syn	3.82	3.89	6.63 <sup>d</sup>	6.45 <sup>d</sup>	7.08 <sup>dd</sup>	9.6	2.2	6.89-7.06 <sup>m</sup>	6.52 <sup>bcd</sup>	5.08 <sup>d</sup>	-	-	-	6.3	-	-	-	-	1.5	-	-
	anti	3.78	3.89	6.28 <sup>d</sup>	6.51 <sup>d</sup>	7.52 <sup>ddd</sup>	9.6	2.2	6.89-7.06 <sup>m</sup>	6.60 <sup>bcd</sup>	5.07 <sup>d</sup>	-	-	-	6.3	-	-	-	-	1.5	-	-
6a	syn	3.82	3.89	6.63 <sup>d</sup>	6.46 <sup>d</sup>	7.08 <sup>dd</sup>	9.6	2.2	6.90-7.06 <sup>m</sup>	-	5.08	-	-	-	-	-	-	-	-	-	-	-
	anti	3.78	3.89	6.28 <sup>d</sup>	6.51 <sup>d</sup>	7.52 <sup>ddd</sup>	9.6	2.2	6.90-7.06 <sup>m</sup>	-	5.07	-	-	-	-	-	-	-	-	-	-	-
5b	syn	3.76	3.87	6.53 <sup>d</sup>	6.42 <sup>d</sup>	7.03 <sup>dd</sup>	9.6	2.2	6.83-7.02 <sup>m</sup>	6.37 <sup>d</sup>	5.35 <sup>ddq</sup>	-	-	1.64 <sup>d</sup>	8.2	6.6	-	-	-	1.7	-	-
	anti	3.76	3.87	6.22 <sup>d</sup>	6.46 <sup>d</sup>	7.44 <sup>ddd</sup>	9.6	2.2	6.83-7.02 <sup>m</sup>	6.44 <sup>d</sup>	5.43 <sup>dd</sup>	-	-	1.61 <sup>d</sup>	8.2	6.6	-	-	-	1.7	-	-
6b	syn	3.75	3.86	6.54 <sup>d</sup>	6.41 <sup>d</sup>	7.02 <sup>dd</sup>	9.6	2.2	6.83-7.02 <sup>m</sup>	-	5.37 <sup>d</sup>	-	-	1.63 <sup>d</sup>	-	6.4	-	-	-	-	-	-
	anti	3.75	3.86	6.23 <sup>d</sup>	6.45 <sup>d</sup>	7.44 <sup>ddd</sup>	9.6	2.2	6.83-7.02 <sup>m</sup>	-	5.43 <sup>d</sup>	-	-	1.61 <sup>d</sup>	-	6.4	-	-	-	-	-	-
5c	syn	3.73	3.88	6.5 <sup>h</sup>	6.43 <sup>d</sup>	7.06 <sup>dd</sup>	9.6	2.2	6.86-7.04 <sup>m</sup>	6.33 <sup>d</sup>	6.45 <sup>d</sup>	-	-	3.8-4.01 <sup>m</sup>	8.5	7.0, 4.4	11.8	-	-	3.21 <sup>bs</sup>	-	
	anti	3.77	3.88	6.23 <sup>d</sup>	6.46 <sup>d</sup>	7.42 <sup>ddd</sup>	9.6	2.2	6.86-7.04 <sup>m</sup>	6.45 <sup>d</sup>	6.45 <sup>d</sup>	-	-	5.12-5.23 <sup>m</sup>	-	-	-	-	-	-	-	
6c	syn	3.72	3.86	6.52 <sup>d</sup>	6.40 <sup>d</sup>	7.03 <sup>dd</sup>	9.6	2.2	6.81-7.02 <sup>m</sup>	-	5.18-5.25 <sup>m</sup>	-	-	3.80-4.01 <sup>m</sup>	-	7.0, 4.0	11.8 <sup>d</sup>	-	-	-	3.64 <sup>bs</sup>	
	anti	3.74	3.86	6.25 <sup>d</sup>	6.43 <sup>d</sup>	7.44 <sup>ddd</sup>	9.9	2.2	6.81-7.02 <sup>m</sup>	-	5.18-5.25 <sup>m</sup>	-	-	3.80-4.01 <sup>m</sup>	-	7.0, 4.0	11.8 <sup>d</sup>	-	-	-	3.64 <sup>bs</sup>	
5d	syn	3.73	3.89	6.48 <sup>d</sup>	6.44 <sup>d</sup>	7.05 <sup>dd</sup>	9.9	1.8	6.86-7.04 <sup>m</sup>	6.33 <sup>d</sup>	5.15 <sup>d</sup>	-	-	-	8.5	-	-	-	1.7	-	3.22 <sup>h</sup> , 3.17 <sup>bs</sup>	
	anti	3.77	3.89	6.25 <sup>d</sup>	6.46 <sup>d</sup>	7.42 <sup>ddd</sup>	9.6	1.8	6.86-7.04 <sup>m</sup>	6.46 <sup>d</sup>	5.18 <sup>d</sup>	-	-	-	9 <sup>h</sup>	-	-	-	1.7	-	3.22 <sup>h</sup> , 3.17 <sup>bs</sup>	
5d <sup>§</sup>	syn	3.74	3.89	6.52 <sup>d</sup>	6.45 <sup>d</sup>	7.04 <sup>dd</sup>	9.6	1.8	6.86-7.04 <sup>m</sup>	6.33 <sup>d</sup>	5.19 <sup>d</sup>	-	-	-	8.5	-	-	-	1.7	-	-	
	anti	3.77	3.89	6.25 <sup>d</sup>	6.44 <sup>d</sup>	7.42 <sup>ddd</sup>	9.6	1.8	6.86-7.04 <sup>m</sup>	6.47 <sup>d</sup>	5.22 <sup>d</sup>	-	-	-	8.5	-	-	-	1.7	-	-	

<sup>†</sup> Shifts are relative to TMS; d, t, q, dd, ddd, m have standard meanings, b = broadened.

<sup>‡</sup> Numbering assigned arbitrarily to H-2 being syn to the side chain.

<sup>§</sup> Solvent: CDCl<sub>3</sub> + HOAc.

<sup>¶</sup> In addition, Proton H-3 (dd, J<sub>3,4</sub>=9.9, J<sub>3,5</sub>=11.8, J<sub>3,5</sub><0.5 Hz).

<sup>||</sup> Observable only after D<sub>2</sub>O exchange.

<sup>∞</sup> Overlapping peaks.

<sup>✓</sup> Weak coupling observed from line broadening and line shape.

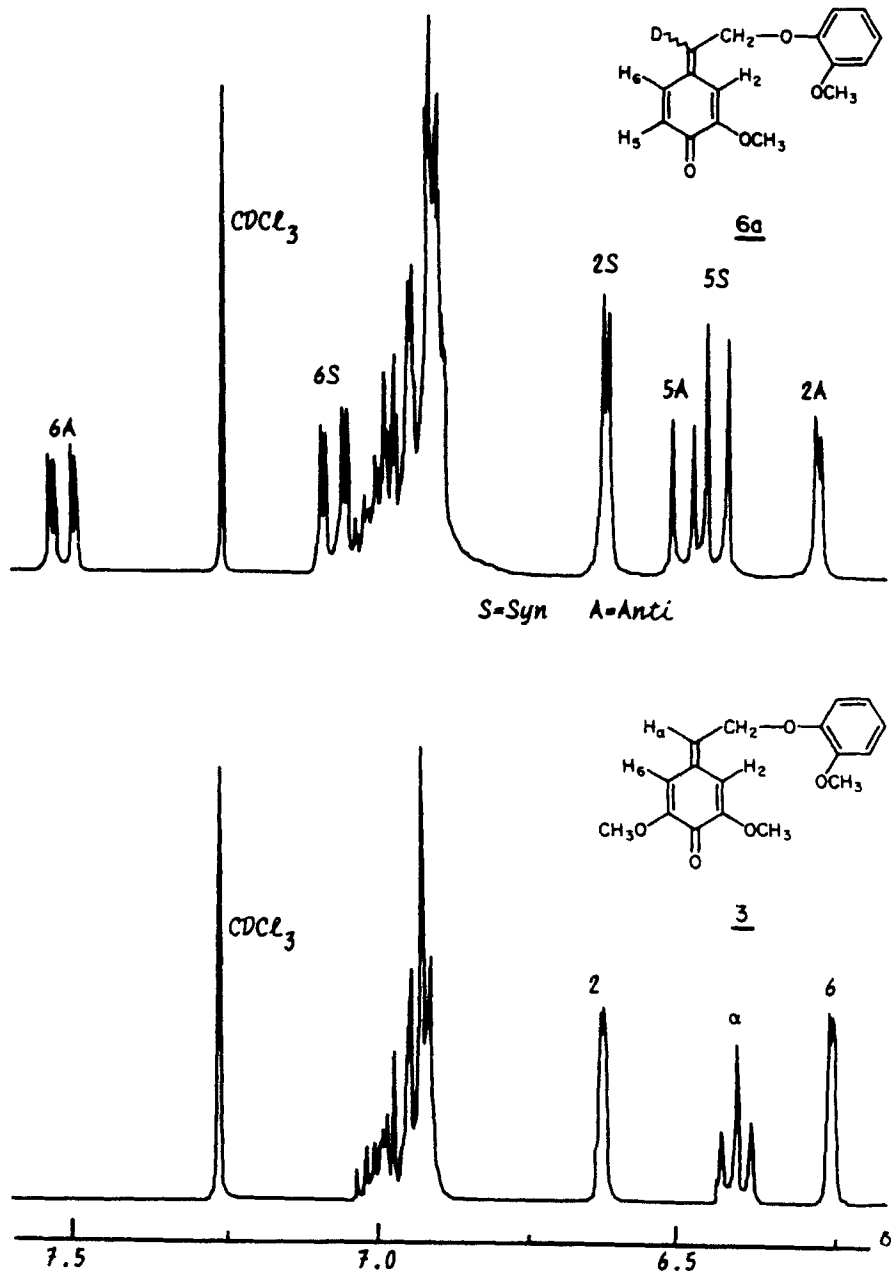


FIGURE 1. Partial  $^1\text{H}$  NMR spectra of **6a** and **3**.

In the symmetrically dimethoxylated quinone methides 2 and 3, and the unsubstituted compound 4, geometric isomers cannot occur, but the steric compression is still encountered as can be inferred from the difference in chemical shift between the otherwise structurally identical H-2's and H-6's (Table 1, Fig. 1).

Splitting due to long-range coupling<sup>13</sup> ( $J^4 < 1$  Hz) observed between H-6 and H- $\alpha$  in the anti-isomers (Fig. 2) of 5a, 5b, 5c, and 5d (Table 1) disappears with  $\alpha$ -deuteration. The coupling is not clear in symmetrical quinone methides 2, 3 and 4 due to more predominant  $H_2-H_\alpha$  coupling, as also observed in the syn-isomers of 5a and 5b. In addition,  $H_5-H_\alpha$  coupling in the anti-isomers ( $J^5 < 0.5$  Hz) is manifested by the slight broadening of the H-5 (anti) resonances. Long range couplings in similar structural types have been noted previously.<sup>13</sup>

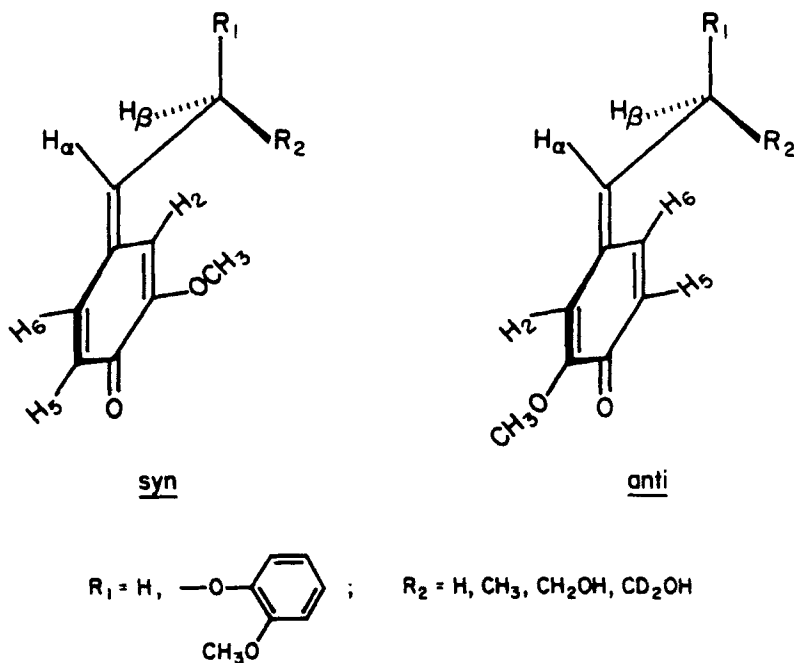


FIGURE 2. Syn and Anti Isomers of Guaiacyl Quinone Methides.

Additional evidence for the assignment of proton signals in the  $^1\text{H}$  NMR spectra of the syn- and anti-quinone methides was obtained from the results of nuclear Overhauser effect (NOE)<sup>5</sup> experiments, in which enhancements in the integrated intensity of  $^1\text{H}$  NMR absorptions were induced by irradiation (to saturation) of spatially close protons. If the protons irradiated are not coupled, energy cannot be dissipated through the bonds but may occur through space by dipole-dipole interactions. Therefore, deuterium labelling at the  $\alpha$ -position in 6a was employed to isolate the  $\beta$  protons. A 50% enhancement is the theoretical maximum for  $^1\text{H}$ - $^1\text{H}$  homonuclear NOE.<sup>14</sup> Irradiation to saturation of the  $\beta$ -protons in 6a resulted in a 25% enhancement of the H-2 signal in the syn-form and of the H-6 signal in the anti-form, whereas the resonances for H-6(syn) and H-2(anti) were not enhanced. Saturation of the single  $\beta$ -proton in 6b gave a 33% enhancement.

Additional NOE experiments provided evidence regarding the orientation of the guaiacyl (G) substituent in quinone methides 6 (and hence in 5 also). For rotation about the  $\alpha$ - $\beta$  bond (Fig. 5), the three staggered rotomers A, B and C represent energy minima. Conformations in which  $\beta$ -substituents (H, R or G) are eclipsed with the quinone methide double bond are clearly high energy transition states because of the severe clash between the eclipsed substituent and H-2 (syn-isomer) or H-6 (anti-isomer) on the quinone methide ring -- even for R = H in the staggered conformation A, the  $\beta$ -protons clash with the quinone methide ring protons (Figures 2 and 3) as perceived from the  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts and the NOE enhancements.

Of the three possible rotomers in Fig. 5, A would undoubtedly be the most likely if R = H, simply based on steric requirements. However, if R is a larger group such as methyl or hydroxymethyl, the choice is not as clear between A and B; rotomer C is the least likely due to steric crowding.



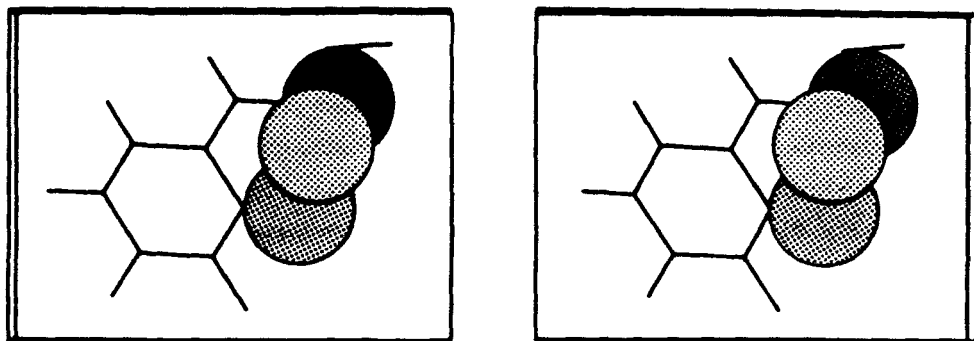


FIGURE 3. Stereographic Projection of Quinone Methide 5a.

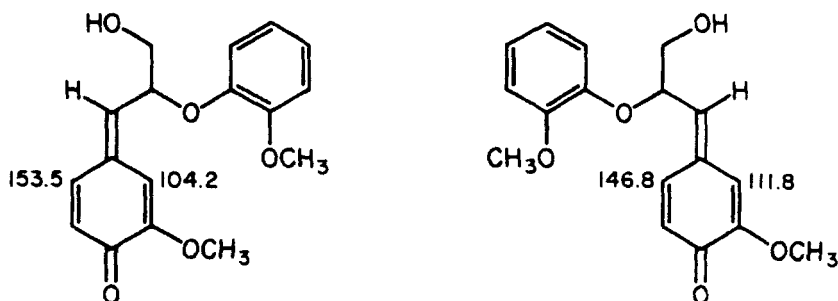


FIGURE 4.  $^{13}\text{C}$  NMR chemical shifts of C-2 and C-6 in syn- and anti-5c.

The  $H_{\alpha}$ - $H_{\beta}$  coupling constants do not allow differentiation among the three possible rotomers since, for C=CH-CH systems, the coupling constants corresponding to  $0^{\circ}$  and  $120^{\circ}$  dihedral angles are very similar.<sup>15</sup> Evidence that A remains the major conformer for 6b was obtained by NOE experiments involving saturation of the 2- and 6-protons in the quinone methide ring. This saturation resulted in a 15-19% enhancement of the methyl signal, indicating its proximity to these protons. In addition, the coupling constants for the side-chain protons were not affected by the presence of acetic acid,  $\text{DMSO-d}_6$ , or  $\text{D}_2\text{O}$ , indicating that the conformation is not solvent dependent. Nor were the  $H_{\alpha}$ - $H_{\beta}$

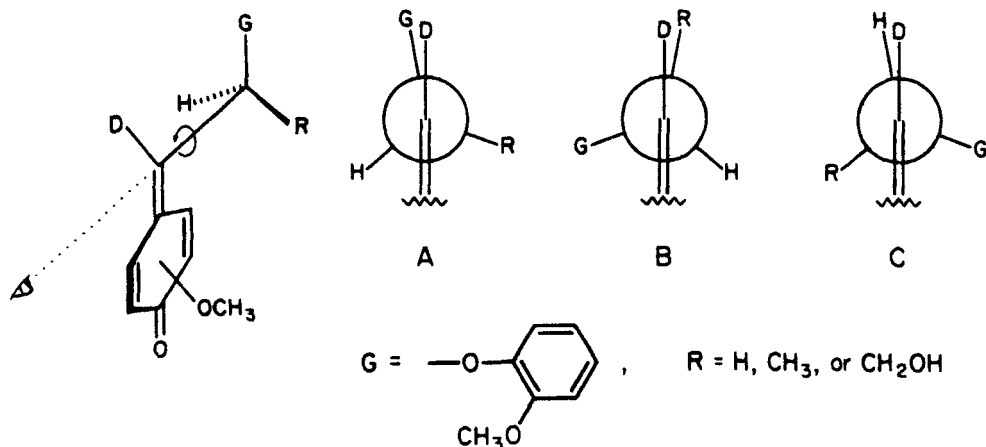


FIGURE 5. Major rotomers of quinone methides.

coupling constants in 5a temperature-dependent over the range  $-40^{\circ}$  to  $+30^{\circ}C$ . The predominance of rotomer A is consistent with the formation of almost exclusively threo-isomers by nucleophilic addition of a variety of compounds ( $R_2NH^4$ ,  $AHQ^{1-2}$ , and anthranol<sup>1-2</sup>) to the quinone methides, 5b and 5c.

#### EXPERIMENTAL

Lignin Models: The precursors of the quinone methides were all lignin models prepared according to literature procedures.<sup>16-19</sup> The  $\gamma$ -dideuterohydroxymethyl model (precursor of 5d) was prepared via the  $\gamma$ -ester<sup>19</sup> with lithium aluminodeuteride (LAD). All  $\alpha$ -deutero models were prepared by LAD reduction of the corresponding  $\alpha$ -ketones.

Quinone Methides: Quinone methides were prepared<sup>4</sup> in small volumes of  $CDCl_3$  and transferred to an NMR tube. All solutions were found to be uncontaminated by products other than  $Me_3SiOSiMe_3$  from the bromination reaction and TMS added as internal standard. NMR tubes were stored in dry ice-acetone until required. Samples for NOE experiments were degassed by the

freeze-thaw method<sup>5</sup> at 0.2 torr or lower. <sup>1</sup>H NMR spectra were run on a Bruker WH270 FT spectrometer using 16K data points (resulting in J values accurate to  $\pm 0.4$  Hz). NOE experiments were performed under gated conditions using 8K data points (to lessen T<sub>1</sub> relaxation effects). The appropriate protons were saturated by irradiating at approx. 80% of normal decoupling power for 6 seconds, normal spectrum acquisition was carried out, and the cycle repeated after a 6-second (2-3 times T<sub>1</sub>) delay time. Integrations were compared with those from a blank experiment run with the irradiating frequency set to an area of the spectrum containing no resonances.

The <sup>13</sup>C NMR of 70 mg of 5c was run in CDCl<sub>3</sub> in a 10 mm tube on a JEOL FX200 FT instrument (50.1 MHz) over 3 h. The following assignments were made by comparison with lignin model spectra<sup>3,16</sup> and from correlation tables in reference 20.

syn-5c:  $\delta$  55.2, 56.0 (methoxyls), 64.8 (C- $\gamma$ ), 79.8 (C- $\beta$ ), 128.5 (C- $\alpha$ ); 140.9, 104.2, 134.1, 181, 132.6, 153.5 (C-1 to C-6 resp.); 151.1, 146.9, 112.6, 124.1, 121.4, 119.5 (C-1' to C-6' resp.).

anti-5c:  $\delta$  55.2, 56.0 (methoxyls), 65.1 (C- $\gamma$ ), 79.5 (C- $\beta$ ), 129.7 (C- $\alpha$ ); 141.3, 111.8, 134.1, 181, 134.0, 146.8 (C-1 to C-6 resp.); 152.8, 146.9, 112.6, 124.1, 121.4, 119.8 (C-1' to C-6' resp.).

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