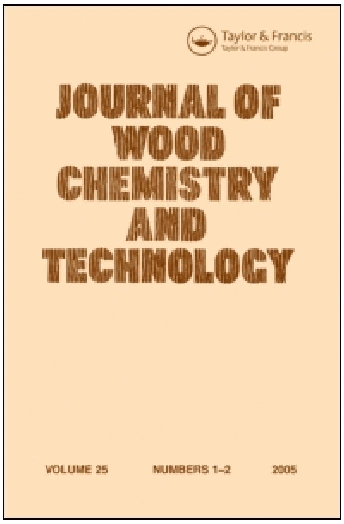

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ADDUCTS OF ANTHRAHYDROQUINONE AND ANTHRANOL WITH LIGNIN MODEL QUINONE METHIDES. 9,10-^{13}C LABELLED ANTHRANOL-LIGNIN ADDUCTS; EXAMINATION OF ADDUCT FORMATION AND STEREOCHEMISTRY IN THE POLYMER

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ABSTRACT

Threo and erythro isomers of 3-acetoxy-1-(4-acetoxy-3-methoxyphenyl)-1-(9,10-dihydro-10-hydroxy-9-oxoanthracen-10-yl)-2-(2-methoxyphenoxy)-propane 8 have been synthesized. These compounds are appropriate model compounds for adducts between anthranol (9-hydroxyanthracene) and quinone methides of β-aryl ether units in the lignin polymer. Adducts of this type are believed to result from side reactions during the anthraquinone-accelerated pulping of wood and may contribute to extensive losses of anthraquinone from the pulping system. The ^{13}C NMR chemical shifts of C-10 in the threo and erythro isomers of 8 are 44.1 and 47.5 ppm relative to tetramethylsilane. Peaks with corresponding chemical shifts appeared in a spectrum of an acetylated adduct prepared from lignin and 9,10-^{13}C labelled anthranol. As in model systems the threo isomer predominated.

+ Maintained at Madison, WI, in cooperation with the University of Wisconsin.

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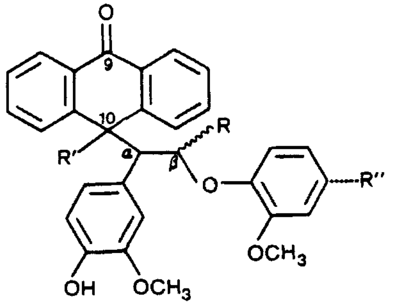
INTRODUCTION

The rate increase in alkaline delignification of wood induced by catalytic quantities of anthraquinone (AQ) has been the subject of considerable investigation. Because of the complex and irregular nature of the lignin polymer,[1-2] appropriate lignin models have been widely used in mechanistic studies. This model work has allowed the elucidation of the major mechanisms contributing to the accelerated delignification.[3-4] However it is important to determine to what extent reactions on the lignin polymer itself are analogous with model reactions.

The proposal[3,5] that anthrahydroquinone (AHQ) is the active species which attacks quinone methides of free phenolic β-ether structures in the lignin molecule is now widely accepted as the main reaction leading to bond cleavage. Preparation and characterization of adducts of type 1 and their derivatives has been the theme of this series.[6-9] It is postulated that formation of these adducts precedes bond cleavage in the lignin molecule during alkaline pulping in the presence of AQ.

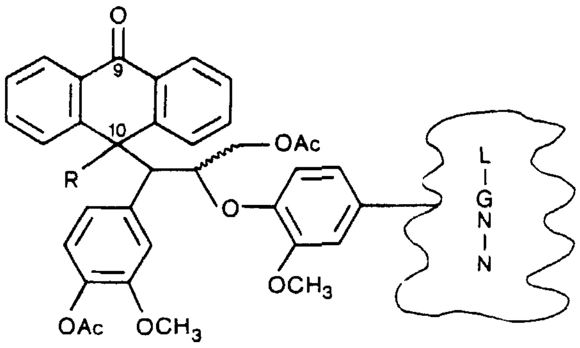


R' = H, OH
R = H, CH_3, CH_2OH
R'' = H, Lignin

1

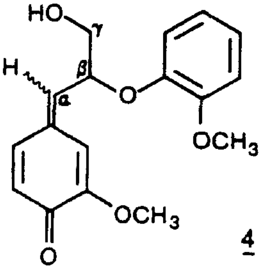
Parallel reactions have used anthranol, the vinylogous enol of anthrone, which adds to quinone methides in an analogous fashion.[3,6,10] This results in analogous adducts in which the subsequent Grob fragmentation cannot occur (R' = H rather than R' = OH in 1) and the adducts are therefore considerably more stable, which is why anthranol adducts were chosen for this study.

Proton and low field ^{13}C NMR evidence for the formation of adducts of type 1 (R" = lignin) between anthranol or AHQ and lignin have already been presented.[11] In that study, acetylated milled wood lignin from loblolly pine was treated with 9,10-^{13}C labelled anthranol or AHQ in dioxane-base at, or slightly below, room temperature. This procedure preferentially hydrolyses the phenolic acetate and, if an α-OAc group is present, allows formation of the quinone methide *in situ* at room temperature or below. The resulting product was acetylated to give adducts 2 or 3 (the 10-OH group in 3 is not acetylated[6]).



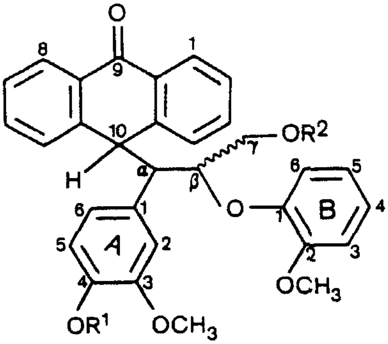
2 R = H
3 R = OH

The 15 MHz ^{13}C NMR spectra[11] of the acetylated adducts 2 or 3 showed evidence for the incorporation of the ^{13}C labels, and the chemical shifts of the 9 and 10 carbons of the anthracenyl moiety were similar to those of the model adducts. Since that communication,[11] the model adducts have been extensively studied and it has been shown that, in aqueous base or in pyridine/chloroform, AHQ or anthranol react in high yield with quinone methide 4 to give solely the *threo* (as defined in reference 6) adduct isomer.[6-10] Smaller nucleophiles, such as methylamine, also give predominantly the *threo* isomer.[12] Conformational studies, using proton NMR, on a series of quinone methides indicated[13] that they exist in relatively rigid rotameric forms which are consistent with the addition of nucleophiles to give products of the observed stereochemistry.



4

Recently we reported on the synthesis of both adduct isomers with the phenolic OH methylated (e.g., 6).[8] It was observed that the ^{13}C NMR chemical shifts of C-10 in the *threo* and



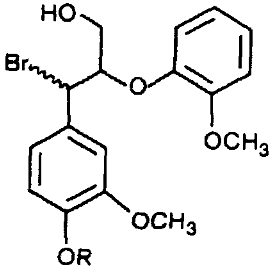
	R^1	R^2
5	H	H
6	Me	H
7	CH_2Ph	H
8	Ac	Ac

erythro forms differed markedly. However, strictly speaking, model 6 does not possess the correct substitution to relate it to the acetylated lignin preparations; the acetylated adducts *threo-* and *erythro*-8 are required.

It was the aim of the present study to compare ^{13}C NMR chemical shifts in the appropriately substituted and derivatized model adducts 8 with those in the higher field ^{13}C NMR spectra of lignin-anthranol adducts and also to provide evidence for the stereoselectivity of reactions occurring in the lignin polymer.

SYNTHESIS OF ADDUCTS

Threo-5 was conveniently prepared in essentially quantitative yield from anthranol and quinone methide 4 as described previously.[6] *Threo*- and *erythro*-6 (with the phenolic OH methylated) were previously prepared in a 2:1 ratio by alkylation of TMS-anthranol [9-(trimethylsiloxy)-anthracene] by the bromide 10 in chloroform in the presence of ZnBr$_2$.[8] It was anticipated that the parent adducts *threo*- and *erythro*-5 could be similarly obtained *via* the benzylated bromide 11. Indeed, this reaction using γ,γ-dideutero-11[14] gave, not only the benzylated adducts *threo*- and *erythro*-γ,γ-dideutero-7 (19% : 14%) but also the parent adducts *threo*- and *erythro*-γ,γ-dideutero-5 (35% : 20%), which resulted from debenzylation reactions occurring under the reaction conditions. The total yield of products 5 and 7, after purification, was 88%. Subsequently it was found that protection of the 4-phenolic group was not necessary, and *threo*- and *erythro*-5 (60 : 40) were obtained in 88% yield from 9 and TMS-anthranol under the same conditions. The reactions were conveniently done in CDCl$_3$ in an NMR tube and monitored by ^{1}H NMR spectroscopy.



9 R = H
10 R = CH$_3$
11 R = CH$_2$Ph

The preparation of the 9,10-^{13}C labelled anthranol-lignin adduct from loblolly pine milled wood lignin was described previously.[11]

^{13}C NMR SPECTRA

^{13}C NMR has proven to be the most valuable technique for obtaining detailed structural information on the complex and irregular lignin polymer.[10,15-21] Solvent peaks from acetone-d_6 are in a more acceptable region of the acetylated lignin spectrum than $CDCl_3$ peaks are and, since small chemical shift differences in model adducts 6 were noted[8,10] between the two solvents, all spectra have been recorded in acetone-d_6.

The 50 MHz ^{13}C NMR spectrum of the acetylated anthranol-lignin adduct is given in Figure 1. An expanded spectrum and a spectrum of the unreacted acetylated milled wood lignin for comparison[10] are available from the authors as Supplementary Material. Large peaks corresponding to the labelled C-9 and C-10 positions of the anthracenyl moiety are evident (shaded) in regions of the spectrum where no significant peaks occur in acetylated milled wood lignin. The multiplicity of peaks in the C-10 region is evidence that quinone methides from other than β-aryl ether units are capable of trapping anthranol.[11] A small but readily apparent reduction in the intensity of peaks 29 and 30 (attributable to Cβ and Cα in β-aryl ether units) is entirely consistent with the reactions involved in formation of the anthranol lignin adduct. Those β-ethers which had free phenolic groups (prior to acetylation) are the ones which would form quinone methides and trap anthranol. Hence, the reduction in the intensity of these lines may be directly attributable to the 'loss' of free phenolic β-aryl ether units. Estimates for the free phenolic content of milled wood lignins vary between 10%[22] and 30%[2] and depend on the lignin isolation method. The relative intensity of the phenolic acetate carbonyl peak, 3b,

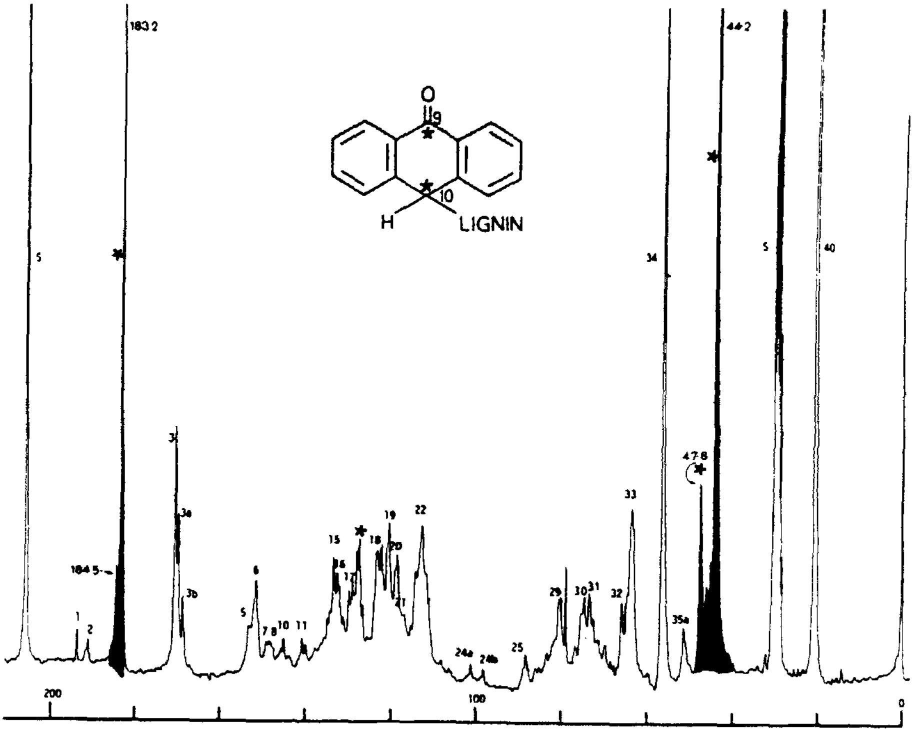


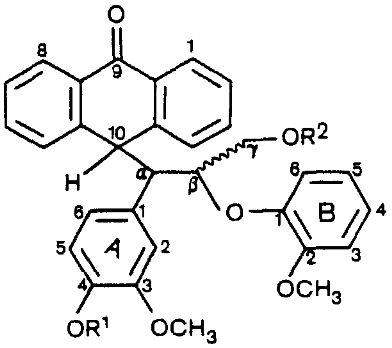
FIGURE 1

is similar to that in the acetylated milled wood lignin. However, adduct formation does not change the number of free phenolic groups and, at least in model compounds, the phenolic acetate carbonyl chemical shift is not significantly altered by adduct formation. The spectrum of the adduct, Figure 1 and Supplementary Material, otherwise closely resembles that of acetylated milled wood lignin.

Table 1 lists the ^{13}C NMR chemical shifts of model adducts; the underivatized adduct 5, the methylated derivative 6,[8] and the acetylated derivative 8. Compound 8 has the appropriate

TABLE 1

^{13}C NMR Chemical Shifts of Aliphatic Carbons in Model Adducts 5, 6, and 8 and in Lignin Adduct 2: Solvent, Acetone-d_6



	5		6		8		2	
	R^1 = H, R^2 = H		R^1 = Me, R^2 = H		R^1 = Ac, R^2 = Ac		Acetylated lignin adduct	
	T	E	T	E	T	E	T	E
10	44.4	47.5	44.4	47.4	44.1	47.5	44.2	47.6
9	183.5	184.6	183.3	184.4	183.0	184.5	183.2	184.5
α	58.8	59.9	58.8	59.8	59.9	60.5	-	-
β	81.1	80.4	81.1	80.4	76.8	76.5	-	-
γ	61.9	61.7	61.7	61.7	64.5	64.5	-	-
OMe	56.8	56.2	56.8	56.2	56.6	56.1	-	-
OMe	56.1	55.9	56.3	56.0	55.7	55.8	-	-
OMe	-	-	55.9	55.7	-	-	-	-

derivatization to closely model the β-aryl ether adducts 2 in the acetylated lignin adducts prepared. It is apparent from Table 1 that the differences between the threo and erythro C-10 chemical shifts noted previously[8] in 6 are also reflected in compounds 5 and 8. In fact, the C-10 chemical shift is influenced only slightly by methylation or acetylation of the phenolic OH or acetylation of the sidechain hydroxymethyl group. Although the chemical shifts of sidechain and methoxyl carbons differ only slightly between the threo and erythro isomers of model adducts 5, 6, and 8 there is a large and consistent difference between the C-10 carbon chemical shifts and, to a lesser extent, the C-9 carbonyls.

The major C-10 peak (δ 44.2) in the acetylated anthranol-lignin adduct spectrum, Figure 1, corresponds well with the shift in threo-8 (δ 44.1, Table 1). As has been observed in model systems, attack of anthranol on quinone methides of this type greatly favours the threo-isomer. There is also a smaller peak at δ 47.6. This cannot necessarily be attributed to the erythro isomer of 2 (cf. compound erythro-8, $\delta_{C-10} = 47.5$) rather than to an adduct from some other non-β-ether quinone methide although the presence of a correspondingly small C-9 carbonyl resonance at δ 184.5 (cf. compound erythro-8, $\delta_{C-9} = 184.5$) strongly suggests that it is. Evidently the reaction in the lignin polymer is less stereoselective than in model systems. Alternatively, the difference may be attributable to the presence of dioxane required to effect solubility in the lignin reaction. Dioxane has peculiar solvating properties which may affect the stereochemical course of the reaction. Indeed the reaction, in dioxane, of oxanthranol (the keto form of AHQ which rapidly generates AHQ^{2-} in base) with a quinone methide similar to 4 but with the hydroxymethyl group acetylated, apparently yields both the threo and erythro adduct isomers.[23] By contrast, in aqueous base or in $CHCl_3$/pyridine only the threo isomer is observed.[6-7,9-10]

In summary, it has been demonstrated that anthranol effectively traps quinone methides generated in the lignin polymer to give adducts analogous to those from lignin model quinone methides. In addition, the threo isomer of the resultant adduct predominates although there is evidence for the formation of minor amounts of the erythro isomer which is not observed in corresponding model systems. This study has demonstrated that reactions using well-chosen lignin model compounds can be extrapolated to the lignin polymer, even to the detail of reaction stereochemistry and provides a further example of the power of ^{13}C NMR to extract detailed structural information from the complex lignin polymer.

EXPERIMENTAL

^{1}H NMR spectra were determined in $CDCl_3$ or acetone-d_6 on a Varian T60, JEOL FX90, Bruker WH270, or Bruker WM250 spectrometer with TMS as internal reference (the 270 MHz spectra were run with 16 K data points resulting in J values accurate to ± 0.4 Hz and the 250 MHz spectra have J values accurate to ± 0.2 Hz). ^{13}C NMR spectra were determined in acetone-d_6 on a JOEL FX90Q (22.5 MHz), Bruker WM250 (62.5 MHz) or JEOL FX200 (50.1 MHz) spectrometer. Proton multiplicities were determined by ^{13}C INEPT using $\tau = 1/4J$ and $\Delta = 3/4J$ (inversion of CH_2 resonances).[24-25] Separate quaternary-carbons-only spectra on the FX90Q were recorded under normal conditions except with the broadband decoupler offset by 5 KHz.[26] Mass spectra were determined with a direct insertion probe on a Hewlett Packard 5985 GC/MS. Melting points were determined on a calibrated Reichert Thermopan mp apparatus. Compounds were purified either by flash chromatography[27] on silica gel using ethyl acetate/petroleum ether as eluant or by thick layer chromatography on silica gel using 5-50% ethyl acetate/petroleum ether as developer. Acetylations were performed with 1/1 acetic anhydride/pyridine (often containing a trace of 4-dimethylaminopyridine as catalyst).

Preparation of Starting Materials

The preparations of lignin models,[10,28] bromides,[8,10,12] quinone methides,[10,12] TMS-anthranol,[8,10] and 9,10-^{13}C labelled anthranol[11] have been described previously.

Preparation of anthranol adducts

The preparations of adduct threo-5 via quinone methide 4,[6] and of threo- and erythro-6 via the bromide 10 and TMS-anthranol[8] have been described previously. Preparation of the 9,10-^{13}C labelled anthranol-lignin adduct from 9,10-^{13}C labelled anthrone and acetylated milled wood lignin was described in reference 11. The polymeric fraction was separated from excess anthranol by size exclusion chromatography.

Alkylation of TMS Anthranol with Bromide 9

1-bromo-1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-propan-3-ol (9) was prepared in $CDCl_3$ in an NMR tube from the corresponding benzyl alcohol (98 mg, 0.31 mmoles) using bromotrimethylsilane[8,12] (49.2 mg, 0.32 mmoles). A large excess (5 eq) of TMS-anthranol[29] and 5 mg of $ZnBr_2$ was added and the tube shaken. Proton NMR indicated that the reaction was complete within 5 minutes. The mixture was transferred to a separatory funnel with $CHCl_3$ and washed with saturated aqueous $NaHCO_3$. The crude product was applied to a preparative tlc plate and eluted several times with 10% EtOAc/PE to remove the anthrone. The remainder, which scarcely moved on the tlc plate was collected and applied to a flash chromatography column.[27] Elution with 2:1 EtOAc/PE cleanly separated the two adduct isomers of 1-(anthracen-9-one-10-yl)-1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propan-3-ol (5), the erythro isomer eluting first.

Erythro-5 (51.7 mg, 34%) was a pale yellow oil; ^1H NMR (90 MHz, acetone-d_6 + 1 drop D_2O) δ 3.30 (t, 1H, $J_{\alpha\beta} = J_{\alpha 10}$ = 6.2, Hα), 3.58 (s, 3H, ring A methoxyl), 3.78 (s, 3H, ring B methoxyl), γ-protons multiplet masked by methoxyls, 4.55 (m, 1H, Hβ), 4.83 (d, 1H, $J_{10\alpha}$ = 6.4, H_{10}), 6.02 (dd, 1H, J_{65} = 8.2, J_{62} = 1.9, H6 ring A), 6.41 (d, 1H, J_{56} = 8.2, H5 ring A), 6.56 (d, 1H, J_{26} = 1.9, H2 ring A), 6.6-8.1 (m, 12H, aromatics): ^{13}C NMR (22.5 MHz, acetone-d_6) Table 1 and Supplementary Material, Table A1. M/S (EI, 70 eV) m/z 467 (.9), 466 (M-H_2C=O, 3), 303 (31), 302 (11), 285 (16), 273 (22), 272 (26), 253 (12), 195 (11), 194 (80), 193 (86), 180 (16), 179 (29), 165 (100), 149 (37), 137 (72), 124 (33), 119 (29), 109 (19), 95 (19), 91 (26), 77 (28). The diacetate, erythro-8, was a pale yellow oil; ^1H NMR (250 MHz, acetone-d_6) δ 1.90 (s, 3H, γ-acetate methyl), 2.19 (s, 3H, phenolic acetate methyl), 3.22 (dd, 1H, $J_{\alpha 10}$ = 7.1, $J_{\alpha\beta}$ = 5.2, Hα), 3.59 (s, 3H, ring A methoxyl), 3.81 (s, 3H, ring B methoxyl), 4.05 (dd, 1H, $J_{\gamma 1\gamma 2}$ = 11.7, $J_{\gamma 1\beta}$ = 5.4, $H\gamma_1$), 4.35 (dd, 1H, $J_{\gamma 2\gamma 1}$ = 11.7, $J_{\gamma 2\beta}$ = 5.0, $H\gamma_2$), 4.80-4.84 (m, 2H, H10 and Hβ, $J_{10\alpha}$ = 7.1 was evident), 6.29 (dd, 1H, J_{65} = 8.1, J_{62} = 1.8, H6 ring A), 6.67 (d, 1H, J_{56} = 8.1, H5 ring A), 6.83 (d, 1H, J_{26} = 1.8, H2 ring A), 6.84-7.04 (m, 4H, ring B protons), 7.17-7.49 (m, 6H, anthracenyl H2-H7), 7.98-8.03 (m, 2H, anthracenyl H1, H8); ^1H NMR (250 MHz, $CDCl_3$) δ 1.87 (s, 3H, γ-acetate methyl), 2.29 (s, 3H, phenolic acetate methyl), 2.81 (dd, 1H, $J_{\alpha 10}$ = 8.8, $J_{\alpha\beta}$ = 3.9, Hα), 3.69 (s, 3H, ring A methoxyl), 3.77 (dd, 1H, $J_{\gamma 1\gamma 2}$ = 11.6, $J_{\gamma 1\beta}$ = 6.8, $H\gamma_1$), 3.85 (s, 3H, ring B methoxyl), 4.25 (dd, 1H, $J_{\gamma 2\gamma 1}$ = 11.6, $J_{\gamma 2\beta}$ = 5.0, $H\gamma_2$), 4.49 (m, 1H, Hβ), 4.62 (d, 1H, $J_{10\alpha}$ = 8.9, H_{10}), 6.45-7.04 (m, 7H, ring A and ring B protons), 7.15-7.46 (m, 6H, anthracenyl H2-H7), 8.13, 8.16 (2 x dd, 2H, J = 7.6, 1.3, anthracenyl H1, H8); ^{13}C NMR (22.5 MHz, acetone-d_6) Table 1 and Supplementary Material, Table A1. M/S (EI, 70 eV), m/z 388 (6), 387 (33), 328 (9), 327 (51), 285 (28), 284 (8), 253 (14), 204 (8), 194 (26), 193 (37), 179 (15), 165 (18), 162 (11), 161 (16), 149 (11), 137 (16), 124 (13), 123 (27), 43 (100).

Threo-5 (81.4 mg, 54%) was a white crystalline solid; mp, ^1H NMR (270 MHz, $CDCl_3$) and ^{13}C NMR (50 MHz, $CDCl_3$)

reported previously (compound 4f, reference 6) and Supplementary Material, Table A1. ^{13}C NMR (62.5 MHz, acetone-d_6) Table 1 and Supplementary Material, Table A1. M/S (EI, 70 eV) m/z 466 (M-H_2C=0, 1), 303 (32), 302 (8), 285 (15), 273 (17), 272 (19), 253 (9), 195 (16), 194 (100), 193 (55), 180 (15), 179 (29), 165 (59), 149 (44), 137 (87), 124 (26), 119 (18), 109 (21), 95 (10), 91 (12), 77 (16). The diacetate, threo-8, was a white crystalline solid (from acetone); mp 183.5-184°C; ^1H NMR (270 MHz, $CDCl_3$ and acetone-d_6) and IR reported previously (compound 4gAc, reference 6); ^{13}C NMR (22.5 MHz, acetone-d_6) Table 1 and Supplementary Material, Table A1. M/S (EI, 70 eV) m/z 388 (15), 387 (65), 328 (22), 327 (100), 286 (10), 285 (58), 284 (14), 254 (6), 253 (25), 222 (8), 204 (14), 203 (36), 195 (10), 194 (64), 193 (76), 179 (29), 165 (41), 163 (11), 162 (15), 161 (34), 137 (26), 124 (14), 123 (40), 121 (21), 119 (12), 95 (14), 91 (10), 77 (13), 43 (67); M/S (CI, methane, 0.5 torr, 35 eV), m/z 581 (M + 1, 6), 388 (4), 387 (7), 328 (5), 327 (37), 285 (5), 223 (5), 205 (11), 195 (34), 194 (10), 193 (10), 163 (38), 161 (5), 153 (3), 126 (4), 125 (100), 124 (3).

Alkylation of TMS-anthranol with Bromide γ,γ-dideutero-11

Alkylation of TMS-anthranol (60 mg, 0.22 m mole) with 1-(4-benzyloxy-3-methoxyphenyl)-1-bromo-3,3-dideutero-2-(2-methoxyphenoxy)propan-3-ol, γ,γ-dideutero-11 (70 mg, 0.17 mmole), gave the expected dideuterated adducts of threo- and erythro-7 along with the debenzylated dideuterated adducts threo- and erythro-5 in a combined yield of 88% after purification by multiple elution preparative thick layer chromatography.

1-(anthracen-9-one-10-yl)-1-(4-benzyloxy-3-methoxyphenyl)-3,3-dideutero-2-(2-methoxyphenoxy)propan-3-ol (γ,γ-dideutero-7). The threo isomer (19 mg, 19%) was a pale yellow oil; ^1H NMR (270 MHz, $CDCl_3$) δ 3.34 (s, 3H, A3 methoxyl), 3.82 (dd, 1H, $J_{\alpha\beta}$ = 11.0, $J_{\alpha 10}$ = 3.3, Hα), 3.97 (s, 3H, B2 methoxyl), 4.56 (d, 1H, $J_{\beta\alpha}$ = 11.0, Hβ), 4.98 (s, 2H, benzyl CH_2), 5.26 (d, 1H, $J_{10\alpha}$

= 3.3, H10), 5.38 (bs, 1H, H2 ring A), 5.40 (bd, 1H, J_{65} = 8.4, H6 ring A), 6.34 (d, 1H, J_{56} = 8.4, H5 ring A), 7.02-7.79 (m, 15H, aromatics), 7.91 (dd, 1H, J = 7.7, 1.1, H8 or H1 anthracenyl), 8.06 (dd, 1H, J = 7.7, 1.1, H8 or H1 anthracenyl). The *erythro*-isomer (14 mg, 14%) was a pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.41 (dd, 1H, $J_{\alpha\beta}$ = 8.1, $J_{\alpha 10}$ = 5.5, Hα), 3.50 (s, 3H, A3 methoxyl), 3.78 (s, 3H, B2 methoxyl), 4.43 (d, 1H, $J_{\beta\alpha}$ = 8.1, Hβ), 4.73 (d, 1H, $J_{10\alpha}$ = 5.5, H10), 5.02 (s, 2H, benzyl CH_2), 5.83 (dd, 1H, J_{65} = 8.1, J_{62} = 1.5, H6 ring A), 6.12 (bs, 1H, H2 ring A), 6.43 (d, 1H, J_{56} = 8.1, H5 ring A), 6.77-7.54 (m, 15H, aromatics), 8.02-8.06 (m, 2H, H1,8 anthracenyl).

1-(anthracen-9-one-10-yl)-3,3-dideutero-1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)propan-3-ol (γ,γ-dideutero-*5*). The *threo*-isomer (30 mg, 35%) was a white crystalline solid with melting point behaviour similar to that of the undeuterated material reported previously (compound *4f*, reference 6); ^{1}H NMR (60 MHz, $CDCl_3$) δ 3.35 (s, 3H, A3 methoxyl), 3.77 (dd, 1H, $J_{\alpha\beta}$ = 10.5, $J_{\alpha 10}$ = 3, Hα), 3.98 (s, 3H, B2 methoxyl), 4.57 (d, 1H, $J_{\beta\alpha}$ = 10.5, Hβ), 5.25 (d, 1H, $J_{10\alpha}$ = 3, H10), 5.3 (partially hidden, phenolic OH), 5.33 (bs, 1H, H2 ring A), 5.40 (dd, 1H, J_{65} = 8, J_{62} = 2, H6 ring A), 6.40 (d, 1H, J_{56} = 8, H5 ring A), 7.0-8.15 (m, 12H, aromatics). The *erythro*-isomer (17 mg, 20%) was a pale yellow oil; ^{1}H NMR (270 MHz, $CDCl_3$ plus 1 drop of D_2O) δ 3.46 (s, 3H, A3 methoxyl), 3.46 (masked, ΣJ = 13.2, Hα), 3.79 (s, 3H, B2 methoxyl), 4.44 (d, 1H, $J_{\beta\alpha}$ = 8.1, Hβ), 4.74 (d, 1H, $J_{10\alpha}$ = 5.1, H10), 5.85 (dd, 1H, J_{65} = 8.1, J_{62} = 1.8, H6 ring A), 5.93 (bs, 1H, H2 ring A), 6.48 (d, 1H, J_{56} = 8.1, H5 ring A), 6.87-8.00 (m, 10H, aromatics), 8.03-8.06 (m, 2H, H1,8 anthracenyl).

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Supplementary Material Available:

Y-expanded ^{13}C NMR spectra of loblolly pine acetylated milled wood lignin and the acetylated 9,10-^{13}C-labelled anthranol-lignin adduct are available from John Ralph at the above address, along with a table of ^{13}C NMR chemical shift assignments for a series of anthranol adduct derivatives.

REFERENCES

1. K.V. Sarkanen and C.H. Ludwig (eds.), "Lignins", Wiley-Interscience, New York, 1971.
2. E. Adler, Wood Sci. Technol. 11, 169 (1977).
3. L.L. Landucci, Tappi 63(7), 95 (1980).
4. J. Gierer, O. Lindeberg, and I. Norén, Holzforschung 33, 213 (1979).
5. J.R. Obst, L.L. Landucci, and N. Sanyer, Tappi 62(1), 55 (1979).
6. L.L. Landucci and J. Ralph, J. Org. Chem. 47, 3486 (1982).
7. J. Ralph and L.L. Landucci, J. Org. Chem. 48, 372 (1983).
8. J. Ralph and L.L. Landucci, J. Org. Chem. 48, 3884 (1983).
9. J. Ralph, L.L. Landucci, B.K. Nicholson, and A.L. Wilkins, J. Org. Chem. 49, 3337 (1984).
10. J. Ralph, Ph.D thesis DA 82-26987, Univ. Microfilms, Ann Arbor, Michigan 48106 (1982).
11. L.L. Landucci, J. Wood Chem. and Technol. 1(1), 61 (1981).
12. J. Ralph and R.A. Young, J. Wood Chem. and Technol. 3(2), 161 (1983).
13. J. Ralph and B.R. Adams, J. Wood Chem. and Technol. 3(2), 183 (1983).

14. The γ,γ-dideuterated model was used primarily because we had it available at the time. It also was of some aid in spectral interpretation.

15. H.H. Nimz, M. Nemr, P. Schmidt, C. Margot, B. Schaub, and M. Schlosser, J. Wood Chem. and Technol. 2(4), 371 (1982).

16. H.H. Nimz, D. Robert, D. Faix, and M. Nemr, Holzforschung 35, 16 (1981) and references therein.

17. V.P-C. Ellwardt, K. Haider, and L. Ernst, Holzforschung 35, 103 (1981).

18. D. Robert and D. Gagnaire, Presented at Eckman Days Symposium, Stockholm, Sweden (1981).

19. H.H. Nimz in "Chemistry of Delignification with Oxygen, Ozone and Peroxides", p. 99, Uni Publishers Co., Tokyo, Japan 1980.

20. H.H. Nimz, Angew. Chem. Int. Edit. Engl. 13(5), 313 (1974).

21. H.H. Nimz, I. Mogharab, and H-D. Lüdemann, die Makromolekulare Chemie 175, 2563 (1974) and references therein.

22. J-M. Yang and D.A.I. Goring, Can. J. Chem. 58, 2411 (1980).

23. O. Lindeberg, J. Gierer, and I. Norén, presented at the 1982 Wood Chemistry Symposium, Niagra Falls, Ontario, and private communication.

24. G.A. Morris and R. Freeman, J. Am. Chem. Soc. 101, 760 (1979).

25. D.M. Doddrell and D.T. Pegg, J. Am. Chem. Soc. 102, 6388 (1980).

26 E. Wenkert, A.O. Clouse, D.W. Cochran, and D.M. Doddrell, J. Am. Chem. Soc. 91, 6879 (1969).

27. W.C. Still, M. Kahn, and A. Mitra, J. Org. Chem. 43, 2923 (1978).

28. J. Ralph and R.A. Young, Holzforschung 35, 39 (1981).

29. Excess bromotrimethylsilane reagent, and that liberated in the reaction appear to destroy TMS-anthranol. Therefore, to perform the entire reaction from the bromide, in situ, required a large excess to obtain the high yield. If the bromide is isolated first, 2 equivalents are sufficient.[8]