(m, 2 H), 3.55–3.98 (m, 1 H), 3.03 (br s, 1 H), 1.15–2.25 (m, 6 H); mass spectrum (70 eV), m/e 141; exact mass calcd for $C_7H_{11}NO_2$ 141.0790, found 141.0790.

***cis*-2-(Hydroxyacetyl)cyclopentanol (34)**: mp 62–64 °C; IR (Nujol) 3600–3050, 1710 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 4.50–4.60 (m, 1 H), 4.35 (AB q, 2 H, J = 19 Hz), 3.12 (br s, 1 H), 2.82 (dt, 1 H, J = 9.5, 4.85 Hz), 2.51 (br s, 1 H), 1.60–2.15 (m, 6 H); mass spectrum (70 eV), m/e 144, 126; exact mass calcd for $C_7H_{10}O_2$ ($C_7H_{12}O_3 - H_2O$) 126.0681, found 126.0681.

***cis*-2-Hydroxycyclopentanecarboxylic acid (35)**: mp 53 °C (lit.[20] mp 52–53.4 °C); IR (melt) 3600–2400, 1720 cm^{-1}; NMR ($CDCl_3/D_2O$, 90 MHz) δ 4.33–4.63 (m, 1 H), 2.60–3.00 (m, 1 H), 1.60–2.15 (m, 6 H); mass spectrum (70 eV), m/e 130, 112; exact mass calcd for $C_6H_8O_2$ ($C_6H_{10}O_3 - H_2O$) 112.0524, found 112.0524.

Acknowledgment. We are indebted to the National Institutes of Health (Grant No. HL-20579) and the Ciba-Geigy Corp. for support of these investigations.

Registry No. 1, 75-87-6; 2, 4732-58-5; 3, 4474-18-4; 4, 14442-22-9; 5, 83967-79-7; 6, 83967-80-0; 7, 83967-81-1; 8, 623-33-6; 9, 14337-43-0; 10, 7064-04-2; 10 acid, 10313-27-6; 11, 83967-82-2; 11 acid, 83967-83-3; 12, 83967-84-4; 12 acid, 83967-85-5; 13, 83967-86-6; 13 acid, 83967-87-7; 14, 83967-88-8; 15, 83967-89-9; 15 acid, 83967-90-2; 16, 83967-91-3; 16 acid, 83967-92-4; 17, 52482-08-3; 17 acid, 52482-09-4; 18, 83967-93-5; 18 acid, 83967-94-6; 19, 83967-95-7; 19 acid, 83967-96-8; 20, 83967-97-9; 27, 75233-61-3; 28, 77790-67-1; 29, 83967-98-0; 30, 83967-99-1; 31, 83968-00-7; 32, 83968-01-8; 33, 83670-84-2; 34, 83670-88-6; 35, 17502-28-2; CNO, 14442-19-4; CEFNO, 51983-62-1; hydroxylamine hydrochloride, 5470-11-1; styrene, 100-42-5; 1-octene, 111-66-0; cyclopentene, 142-29-0; cyclohexene, 110-83-8; 1-octyne, 629-05-0; 2,2-dimethyl-4-vinyl-1,3-dioxolane, 83968-02-9; (*E*)-1-(trimethylsilyl)-1-octene, 57365-47-6; (*E*)-2-butene, 624-64-6; (*Z*)-2-butene, 590-18-1; 1-methylcyclopentene, 693-89-0; 2,3-dimethyl-2-butene, 563-79-1; 3-hydroxy-3-phenylpropionitrile, 17190-29-3; 3-hydroxynonanenitrile, 30683-75-1; 2-benzylidene-3-oxononanenitrile, 83968-03-0; 3-(2,2-dimethyl-1,3-dioxolan-4-yl)-3-hydroxypropionitrile, 83679-29-2; *erythro*-2-methyl-3-hydroxybutyronitrile, 83968-04-1; *threo*-2-methyl-3-hydroxybutyronitrile, 83968-05-2; *cis*-2-hydroxycyclopentanecarbonitrile, 70367-34-9; *cis*-2-hydroxycyclohexanecarbonitrile, 70367-35-0; 6-oxoheptanenitrile, 18458-15-6; 2-nitroethanol, 625-48-9; phenyl isocyanate, 103-71-9; methyl 3-hydroxy-3-phenylpropionate, 7497-61-2; methyl 3-hydroxynonanoate, 83968-06-3; methyl *erythro*-3-hydroxy-2-methylbutanoate, 39788-58-4.

(20) Pascual, J.; Castells, J. *J. Am. Chem. Soc.* **1952**, *74*, 2899.

Adducts of Anthrahydroquinone and Anthranol with Lignin Model Quinone Methides. 2. Dehydration Derivatives. Proof of Threo Configuration

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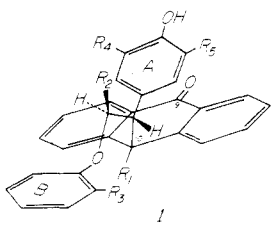
NMR studies of novel dehydration derivatives of anthrahydroquinone (AHQ)–lignin and anthranol–lignin model quinone methide adducts have confirmed the sole diastereomeric form of the adducts as "threo". Upon dehydration of the AHQ adduct 1-(3,4-dimethoxyphenyl)-1-(10-hydroxy-9-oxoanthracen-10-yl)-2-(2-methoxyphenoxy)propane with polyphosphoric acid, the spiro compound 3′-(3,4-dimethoxyphenyl)-2′,3′-dihydro-8′-methoxy-2′-methylspiro[anthracene-9(10*H*),4′-[4*H*-1]benzopyran]-10-one (**3b**) was obtained. Reduction of the anthranol adduct 1-(3-methoxy-4-hydroxyphenyl)-1-(9-oxoanthracen-10-yl)-2-(2-methoxyphenoxy)propane with $LiAlH_4$, followed by dehydration with BF_3·Et_2O gave the bicyclic compound 10,11-dihydro-2,3-dimethoxy-11-[1-(2-methoxyphenoxy)ethyl]-5,10-*o*-benzeno-5*H*-dibenzo[*a*,*d*]cycloheptene (**7d**). Coupling constants of the aliphatic protons in **3b** and **7d** are consistent only with the threo form. Therefore, by analogy, all other reported AHQ and anthranol adducts with asymmetry of Cα and Cβ are assigned the threo configuration.

A previous paper[1] describes the synthesis and characterization of adducts **1** formed by reaction of anthrahydroquinone (AHQ) or anthranol with lignin model quinone methides. Adducts of this type were postulated to be important intermediates in the catalytic delignification of wood. In the compounds where $R^2 \neq H$, both diastereomers are possible, although only one isomer has been found. Our tentative assignment of "threo"[1] is now confirmed by NMR studies of dehydration derivatives of **1** as reported here.



1

Synthesis of Derivatives

Dehydration reactions were performed with the methylated derivatives **2** (Scheme I) by utilizing either polyphosphoric acid (PPA) or boron trifloride etherate (BF_3·Et_2O). Dehydration of **2a** afforded an almost quantitative yield of the spiro product **3a**, presumably by an electrophilic attack of a transient benzylic carbonium ion at C-10 on ring B. Corresponding dehydration of **2b** (R_2 = CH_3) to **3b** was significantly less efficient (38%) perhaps

[†] Maintained at Madison, WI, in cooperation with the University of Wisconsin.

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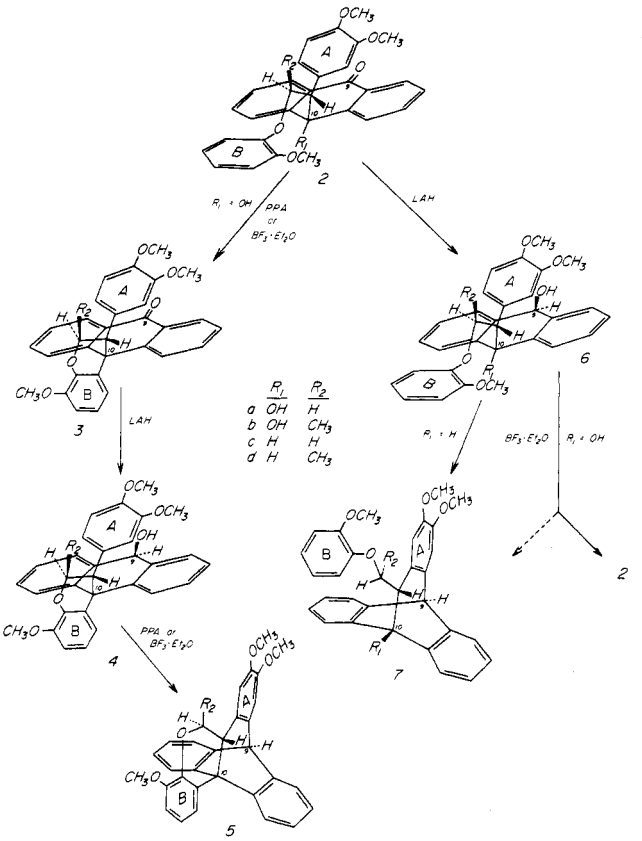
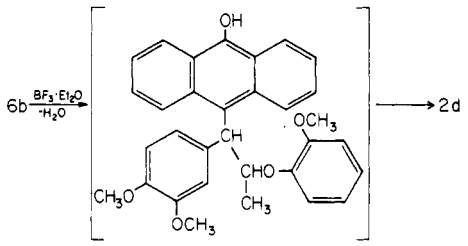
(1) Paper 1: Landucci, L. L.; Ralph, J. *J. Org. Chem.* **1982**, *47*, 3486.

0022-3263/83/1948-0372$01.50/0

Scheme I



Scheme II



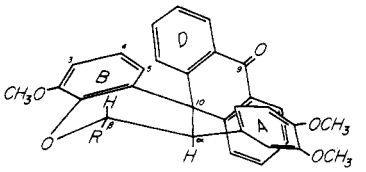
due to steric factors. Reduction of the carbonyl group in **3a** by lithium aluminum hydride ($LiAlH_4$) gave the 9β-alcohol **4a**.[2] Subsequent dehydration with PPA afforded the tricyclo derivative **5a** by electrophilic attack of the C-9 carbonium ion on ring A. This dehydration also occurred quantitatively at room temperature in chloroform solution over a period of 7 months.

With adducts **2c** and **2d** (R_1 = H), formation of spiro products (corresponding to **3**) by dehydration is not possible. However, $LiAlH_4$ reduction of the carbonyl group proceeded as expected, giving **6c** and **6d**, respectively. Dehydration of **6c** with BF_3·Et_2O gave the bicyclo product **7c** which is analogous with the transformation of **4** to **5**. Alternatively, the corresponding product **7d** was prepared by $LiAlH_4$ reduction of the free phenolic analogue of **6d** (4-OH instead of 4-OCH_3 in ring A), followed by BF_3·Et_2O dehydration and diazomethane methylation.

When **6b** (R_1 = OH) was treated with BF_3·Et_2O, the expected dehydration product **7b** was obtained as a minor product. The major product was **2d** which was presumably formed by loss of water across the anthracenyl moiety in **6b** followed by rearrangement of the resulting enol to the more stable keto form (Scheme II).

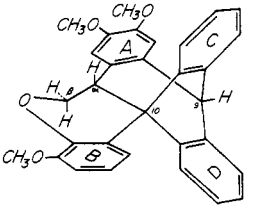
NMR Characterization

In **3a** and **3b**, the coupling constants[3] for the α and β



3a, R = H
3b, R = CH_3

protons (Table I) indicate a pseudochair (or half-chair) conformation. In this structure, ring A is "locked" symmetrically over the anthracenyl moiety, resulting in more intense shielding of the ring A protons as compared to those in the precursor adducts.[1] In addition, unlike the precursors, H5 in the B ring is forced into the shielding region on the opposite side of the anthracenyl moiety. The methyl substituent in **3b** is clearly equatorial as evidenced by the large (11.0 Hz) diaxial Hα–Hβ coupling constant. Consequently, the configuration of **3b** must arise from the threo isomer[4] of **2**. Similarly, the ^1H NMR spectra of the tricyclo derivative **5a** are consistent with a pseudochair



5a

conformation in the pyran ring. Differences in chemical shifts of the β protons between **3a** and **5a** can be explained on examination of Fieser models. Typical shifts for methylene protons in lignin models such as guaiacylglycol β-guaiacyl ether are δ 3.9–4.1.[5] In **3a**, upon rotation of ring A about its axis, both the axial (β_2, Table I) and the equatorial (β_1) protons are deshielded (δ 4.64 and 4.39, respectively). The greater paramagnetic shift of the axial proton results from additional deshielding by ring D. Upon reduction of the carbonyl group in **3a** and subsequent cyclization to **5a**, the axial proton (now β_1)[6] is forced out of the deshielding regions of rings A and D (δ 3.82). Conversely, the equatorial proton in **5a** is deshielded by the now-rigid A ring, resulting in a greater paramagnetic shift (δ 4.57) than in the more flexible **3a**.

Less can be deduced from the bicyclo derivatives **7** since the α–β bond is (in principle) free to rotate. However, the extraordinarily high shieldings of the methyl substituent in **7b** (δ 0.25) and **7d** (δ 0.32) indicate that it is situated between rings A and D. Examination of Fieser models of *erythro*- and *threo*-**7b** indicate that hydrogen bonding between the 10-hydroxyl proton and the guaiacyl oxygen is likely only in the erythro form. The ^1H NMR spectrum

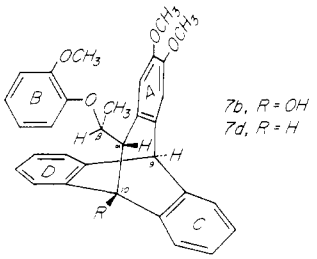
(2) It was shown in ref 1 that adducts such as **2** adopt a conformation in which ring A is centered directly over the anthracenyl ring system. The least hindered approach of the reducing agent is therefore from the opposite side (α face) to give the 9β-alcohol as supported by ^1H NMR spectroscopy. In one case (**4a**), rearrangement occurred in solution over a period of several weeks to give a 60:40 ratio of α to β.

(3) Recently, an empirical method for calculating Karplus curves (which takes into account the electronegatives of the α and β substituents) has been published: Haasnoot, C. A.; Deleeuw, F. A. A. M.; Altona, C. *Tetrahedron* **1980**, *36*, 2783.

(4) "Threo" is assigned in analogy with the parent models; see footnote 18 in paper 1 of this series (ref 1).

(5) Ludwig, C. H.; Nist, B. J.; McCarthy, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 1186.

(6) B_1 is defined as the higher field β proton.



of **7b** shows a typical value (δ 3.34) for the 10-hydroxyl proton in contrast to the general observation of strong intramolecular hydrogen bonding with the guaiacyl oxygen in other AHQ adducts such as **2a** (δ 6.45).[1] This observation is consistent with the threo conformation for **7b**.

In summary, it has been established by high-resolution ^{1}H NMR analysis of dehydration derivatives, and by analogy, that the adducts formed by the reaction of AHQ or anthranol with lignin model quinone methides all have a threo configuration. This significant observation indicates a high degree of stereospecificity in the attack of lignin model quinone methides by large nucleophiles and provides a more complete understanding of novel catalytic systems applicable to the delignification of wood.

Experimental Section

^{1}H NMR spectra[7] were determined in $CDCl_3$ or acetone-d_6 on a Bruker WH270 FT spectrometer with Me_4Si as an internal reference and by using 16K data points (resulting in J values accurate to ±0.4 Hz). ^{13}C NMR spectra[7] were determined methide a JEOL FX60 or a JEOL FX200 FT spectrometer. Infrared spectra of samples in KBr disks or as films were determined on a Beckman IR-12 spectrometer. Mass spectra (EI, probe, 70–80 eV) were determined on a Varian MAT 112 spectrometer (Raltech Scientific Services, Inc.) or on a Finnigan 4510 GC/MS instrument. Elemental microanalyses were performed by Galbraith Laboratories, Inc. Melting points were determined on a calibrated Thomas-Hoover capillary melting point apparatus. Unless otherwise noted, all products exhibited only one spot on thin-layer chromatography (silica gel, 10–50% ethyl acetate/hexane as developer). When required, compounds were purified by thick-layer or column chromatography on silica gel.

Parent Adducts. All parent AHQ- and anthranol–quinone methide adducts (**2**) were prepared as previously described.[1]

General Procedures. No attempt was made to optimize product yields in the following reactions.

(A) Dehydration with Polyphosphoric Acid (PPA). A mixture of the adduct (30–100 mg) and PPA (~5 g) was heated at 100 °C for 1–2 h. The dark mixture was then stirred with water (40 mL) and the resulting suspension extracted with $CHCl_3$ or Et_2O. The organic layer was washed with water and saturated $NaHCO_3$ solution, dried over $MgSO_4$, and evaporated to an oil or solid.

(B) Dehydration with Boron Trifluoride Etherate (BF_3·Et_2O). The adduct (300–100 mg) was dissolved in glacial acetic acid (5 mL). BF_3·Et_2O (1–2 equiv) was added, and the solution was stirred at room temperature for 24 h. The solution was then poured into water (30 mL) and the resulting suspension extracted with ether. The extract was washed with saturated NaCl solution and saturated $NaHCO_3$ solution, dried over $MgSO_4$, and evaporated to an oil or solid.

(C) Lithium Aluminum Hydride Reduction. The ketone (100–200 mg) in anhydrous THF (5 mL) was added dropwise to a suspension of $LiAlH_4$ (2 equiv) in THF (5 mL) and either stirred at room temperature for 12 h or refluxed for 1 h. Excess $LiAlH_4$ was destroyed with 50% aqueous THF, and the aluminum salts were dispersed with saturated sodium potassium tartrate solution. The mixture was extracted with Et_2O, and the extract was washed several times with tartrate solution, dried over $MgSO_4$, and evaporated to an oil or solid.

Specific Derivatives. 3′-(3,4-Dimethoxyphenyl)-2′,3′-dihydro-8′-methoxyspiro[anthracene-9(10*H*),4′-[4*H*-1]benzopyran]-10-one (3a).[7] Dehydration of **2a** according to general procedure A gave **3a** as a yellow oil (98%). Crystallization from acetone gave white crystals: mp 234.5–235 °C; IR (KBr) 1670 (vs, C=O), 1082 cm^{-1} (s, ether in benzopyran ring); ^{1}H NMR (Table I); ^{13}C NMR[7] (50 MHz, $CDCl_3$) δ 51.2 (C_{10}), 55.0 (Cα), 55.6, 55.9, 56.1 (methoxyls), 65.8 (Cβ), 110.0, 110.7, 112.5 (C2,5, ring A; C3, ring B), 120.8–133.8 (Cl,6, ring A; C4,5,6, ring B; Cl–8,8a,9a, anthracenyl), 145.1–151.5 (C3,4, ring A; C1,2, ring B; C4a,10a, anthracenyl); MS, m/e (relative intensity) 478 (100, M$^+$), 356 (8), 327 (37), 314 (66), 229 (30), 271 (20), 255 (18), 164 (31), 149 (57).

***threo*-3′-(3,4-Dimethoxyphenyl)-2′,3′-dihydro-8′-methoxy-2′-methylspiro[anthracene-9(10*H*),4′-[4*H*-1]benzopyran]-10-one (3b).**[7] Dehydration of **2b** according to general procedure A gave crude **3b** which, after preparative TLC, yielded pure product (38%). Crystallization from acetone gave colorless crystals: mp 204.5–205 °C; IR (film) 1672 (vs, C=O), 1382 (w, γ-CH_3), 1084 cm^{-1} (s, ether in benzopyran ring); ^{1}H NMR (Table I);[8] ^{13}C NMR[7] (acetone-d_6) δ 20.8 (γ-CH_3), 52.3 (C10), 55.9, 56.3, 56.5 (methoxyls), 62.9 (Cα), 71.9 (Cβ), 111.8, 112.2 (C2, ring A; C3, ring B), 113.8 (C5, ring A), 121.1–134.4 (C1,6, ring A; C4-6, ring B; C1–8,8a,9a, anthracenyl), 146.7–149.9 (C3,4, ring A; C2, ring B; C4a,10a, anthracenyl), 150.4 (C1, ring B), 182.0 (C9, anthracenyl); MS, m/e (relative intensity) 492 (76, M$^+$), 341 (100), 314 (66), 299 (17), 271 (18), 178 (24).

3′-(3,4-Dimethoxyphenyl)-2′,3′-dihydro-10-hydroxy-8′-methoxyspiro[anthracene-9(10*H*),4′-[4*H*-1]benzopyran] (4a).[7] Reduction of **3a** according to general procedure C gave **4a** as a foamy solid: 91%; mp 190–195 °C. Preparative TLC gave pure **4a**; 86%; IR (KBr) 3535 (m, sharp, OH), 1088 cm^{-1} (s, ether in benzopyran ring); ^{1}H NMR (Table I).

13b,14-Dihydro-1,11,12-trimethoxy-4b,9-*o*-benzeno-9*H*-dibenzo[3,4:6,7]cyclohepta[1,2-*c*][1]benzopyran (5a).[7] Dehydration of **4a** by general procedure A gave **5a** as an amber oil (86%). Crystallization from acetone gave white crystals, mp 137.5–140 °C. The product was also formed in quantitative yield when a solution of **4a** in $CHCl_3$ was kept at room temperature for 7 months: IR (film) 1070 cm^{-1} (s, ether in benzopyran ring); ^{1}H NMR (Table I); ^{13}C NMR[7] (acetone-d_6) δ 46.1 (C9), 51.3 (C10), 54.7 (Cα), 56.3 (methoxyls), 68.3 (Cβ), 111.2–116.3 (C2,5, ring A; C3, ring B), 120.2 (C5, ring B), 123.8 (C4, ring B), 125.2–127.6 (C1–8, anthracenyl), 131.2 (C6, ring B), 135.6 (C1, ring A), 141.8, 142.2 (C8a,9a), 144.7, 145.2 (C4a,10a), 147.4, 148.2, 149.3 (C2, ring B; C3,4, ring A), 150.1 (C1, ring B); MS, m/e (relative intensity) 462 (100, M$^+$), 447 (17), 445 (10), 431 (24), 311 (13). Anal. Calcd for $C_{31}H_{26}O_4$: C, 80.50; H, 5.67. Found: C, 80.35; H, 5.83.

1-(3,4-Dimethoxyphenyl)-1-(9,10-dihydroxyanthracen-10-yl)-2-(2-methoxyphenoxy)ethane (6a). Reduction of **2a** by general procedure C gave a crude product, which, upon preparative TLC, yielded pure **6a** as a colorless oil: 70%;[9] IR (film) 3500 cm^{-1} (br, OH); ^{1}H NMR (Table I); MS, m/e (relative intensity) 287 (13), 286 (5), 211 (6), 210 (5), 209 (4), 194 (11), 193 (10), 164 (100), 149 (31), 123 (12).

***threo*-1-(3,4-Dimethoxyphenyl)-1-(9,10-dihydroxyanthracen-10-yl)-2-(2-methoxyphenoxy)propane (6b).** Reduction of **2b** by general procedure C gave a quantitative yield of **6b** as a white foamy solid (^{1}H NMR, Table I).

1-(3,4-Dimethoxyphenyl)-1-(9-hydroxyanthracen-10-yl)-2-(2-methoxyphenoxy)ethane (6c). Reduction of **2c** by general procedure C gave a yellow-orange oil which, upon preparative TLC, yielded pure **6c**: 55%;[9] IR (film) 3500 cm^{-1} (b, OH); ^{1}H NMR (Table I); MS, m/e (relative intensity) 327 (4), 287 (39), 286 (13), 195 (18), 194 (34), 193 (19), 178 (45), 165 (37), 164 (100), 149 (89), 123 (28).

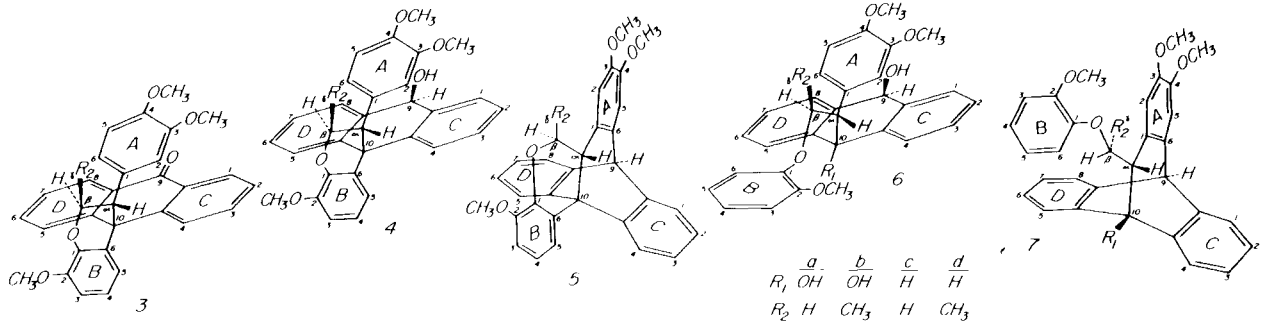
1-(3,4-Dimethoxyphenyl)-1-(9-hydroxyanthracen-10-yl)-2-(2-methoxyphenoxy)propane (6d). Compound **6d** was not prepared specifically but was isolated during the preparation of

(7) To simplify comparisons between various compounds containing different ring systems, all NMR data are reported on the basis of the numbering system of the parent adducts rather than that of the preferred IUPAC name.

(8) This compound and some reported in the previous paper (ref 1) exhibited hindered rotation phenomena which caused line broadening at ambient probe temperature.

(9) The cleavage fragments guaiacol and 3,4-dimethoxystyrene were also found.

Table I. ^{1}H NMR Spectral Data[a]



compd	solv[b]	methoxyls A3	methoxyls A4	methoxyls B2	ring A 2-H	ring A 5-H	ring A 6-H	$J_{5,6}$	$J_{6,2}$	ring B 3-H	ring B 4-H	ring B 5-H	$J_{3,4}$	$J_{3,5}$	$J_{4,5}$	rings C and D 2-7-H	rings C and D 1,8-H
3a	C	3.30	3.72	4.03	5.16 (d)	6.22 (d)	5.31 (dd)	8.5	2.0	6.90 (dd)	6.79 (t)	6.31 (d)	7.9	1.5	7.9	7.21–7.59 (m)	8.02–8.09 (2 dd)
3b[8]	A	3.25 (br s)	3.64	3.95	5.1, 5.5 (br h)	6.35 (br d)	5.1, 5.5 (br h)	8.1	?	6.95 (dd)	6.73 (t)	6.17 (dd)	8.1	1.5	8.1	7.21–7.66 (m)	7.97 (br d)
4a	C	3.30	3.76	4.00	5.31 (br s)	6.40 (d)	5.55 (br s)	8.1	?	6.83 (dd)	6.72 (t)	6.21 (dd)	8.1	1.5	7.7	7.04–7.44 (m)	7.60 (br d)
5a	A	3.69	3.81	3.91	*e*	*e*				6.53							7.46 (m)
6a	C	3.38	3.76	3.93	5.72 (d)	6.44 (d)	5.88 (dd)	8.1	1.8	6.80–7.02 (m)			?	?	?	7.22	8.03 (m)
6b	A	3.38	3.68	3.92	5.97[c]	6.52 (d)	5.95[c]	8.5	?	6.81							8.11 (m)
6c	C	3.40	3.78	3.93	5.74 (d)	6.47 (d)	5.88 (dd)	8.1	1.8	6.92–7.02 (m)			?	?	?	7.20	7.65 (m)
6d	A	3.67	3.82	3.99	6.79												7.81 (m)
7b	C	3.79	3.86	3.92	*e*	*e*				6.81							7.78 (m)
7c	A	3.68	3.82	3.97	*e*	*e*				6.82							7.47 (m)
7d	A	3.73	3.82	3.83	*e*	*e*				6.94							7.57 (m)

compd	solv[b]	9-H	9-OH	10-H	10-OH	α-H	β_1-H[6]	β_2-H	γ-H	J_{α,β_1}	J_{α,β_2}	J_{β_1,β_2}	$J_{\beta,\gamma}$	$J_{10\alpha}$
3a	C					3.54 (a, dd)	4.39 (e, dd)	4.64 (a, dd)		3.7	12.3	11.4		
3b[8]	A					3.24 (d)	4.86 (dq)		1.14 (d)	11.0		5.9		
4a	C	3.58 (br s)	2.00 (br s)			3.46 (a, dd)	4.27 (e, dd)	4.60 (a, dd)		3.3	12.1	11.0		
5a	A	5.06				3.42 (a, dd)	3.82 (a, t)	4.57 (e, dd)		11.0	2.6	11.0		
6a	C	4.01 (br s)	?		5.95 (br s)	3.44 (dd)	4.20 (dd)	4.46 (dd)		4.8	8.5	9.6		
6b	A	?	2.83		6.63	3.36[c]	5.02 (dq)		1.09 (d)	8.5		5.9		
6c	C	3.97[d] (br d)	1.92[d] (br d)	4.87 (d)		3.48 (ddd)	4.14 (dd)	4.37 (dd)		4.8	9.9	9.6		3.7
6d	A	4.93	?	4.81 (d)		3.6[c]	5.07 (dq)		0.65 (d)	6.6		6.6	3.7	
7b	C	4.75			3.34 (br s)	3.62 (d)	5.06 (dq)		0.25 (d)	2.2		6.3		
7c	A	4.94		4.76 (d)		3.6[c]	3.6[c]	4.24 (dd)		?	?	?		3.3
7d	A	4.92		4.50 (d)		3.60 (d)	5.05 (dq)		0.32 (d)	3.7		6.3	4.0	

[a] Chemical shifts are in parts per million relative to Me_4Si and J values are in hertz. Peaks are sharp singlets unless designated otherwise: a = axial, e = equatorial, br = broad, d = doublet, h = hump, s = singlet, t = triplet, m = multiplet, q = quartet. [b] C = $CDCl_3$ and A = acetone-d_6. [c] Overlapping peaks. [d] Values obtained from 60-MHz spectra; $J_{9H,9OH}$ = 10 Hz. [e] With other aromatics.

7d (see below): ^{1}H NMR (Table I); MS, *m/e* (relative intensity) 478 (M - H_2O, 10), 355 (57), 327 (100), 326 (33), 295 (35), 265 (11), 253 (14), 252 (16), 239 (13), 178 (16), 151 (19).

***threo*-10,11-Dihydro-2,3-dimethoxy-11-[1-(2-methoxyphenoxy)ethyl]-5,10-*o*-benzeno-5*H*-dibenzo[*a*,*d*]cyclohepten-10-ol (7b).**[7] Dehydration of **6b** by general procedure B gave predominantly **2d** (38%) and only a 5% yield of expected product **7b**: ^{1}H NMR (Table I); MS, *m/e* (relative intensity) 494 (M^+, 1), 371 (27), 370 (49), 343 (32), 342 (45), 341 (100), 325 (13), 315 (18), 311 (20), 165 (28), 151 (17).

10,11-Dihydro-2,3-dimethoxy-11-[(2-methoxyphenoxy)methyl]-5,10-*o*-benzeno-5*H*-dibenzo[*a*,*d*]cycloheptene (7c).[7] Dehydration of **6c** by general procedure B gave a crude product (90%) which, upon column chromatography, yielded pure **7c**: 72%; colorless oil; IR (film), no OH or C=O absorbance; ^{1}H NMR (Table I); ^{13}C NMR[7] (acetone-d_6) δ 44.7 (C10), 47.3 (C9), 54.9 (Cα), 56.3 (methoxyls), 72.9 (Cβ), 113.2-117.2 (C2,5, ring A; C3,6, ring B), 121.7, 122.1 (C4,5, ring B), 125.2-149.3 (C1,3,4,6, ring A; C2, ring B; C1-8,4a,8a,9a,10a, anthracenyl), 150.9 (C1, ring B); MS, *m/e* (relative intensity) 464 (M^+, 19), 341 (100), 327 (29), 326 (13), 310 (16), 309 (11), 295 (23), 252 (12), 239 (10), 178 (13), 163 (29).

***threo*-10,11-Dihydro-2,3-dimethoxy-11-[1-(2-methoxyphenoxy)ethyl]-5,10-*o*-benzeno-5*H*-dibenzo[*a*,*d*]cycloheptene (7d).**[7] Reduction of the free phenolic analogue of **2d**, 1-(3-methoxy-4-hydroxyphenyl)-1-(9-oxoanthracen-10-yl)-2-(2-methoxyphenoxy)propane, by general procedure C gave a 91% yield of the corresponding alcohol, 1-(3-methoxy-4-hydroxyphenyl)-1-(9-hydroxyanthracen-10-yl)-2-(2-methoxyphenoxy)propane: MS, *m/e* (relative intensity) 464 (M - H_2O, 2), 341 (23), 313 (34), 312 (12), 287 (51), 194 (41), 193 (68), 178 (21), 165 (40), 164 (63), 163 (100), 151 (31), 124 (19). Dehydration of the alcohol obtained above by general procedure B (6 h) and subsequent methylation with diazomethane gave **6d** (30%) and the expected product **7d**: 31%; IR (film), no OH or C=O absorptions; ^{1}H NMR (Table I); MS, *m/e* (relative intensity) 478 (30, M^+), 355 (95), 327 (100), 295 (28), 151 (12).

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Registry No. **2a**, 74838-65-6; **2b**, 82247-06-1; **3a**, 84064-76-6; **3b**, 84064-68-6; **4a**, 84064-69-7; **5a**, 84064-70-0; **6a**, 84064-71-1; **6b**, 84064-72-2; **6c**, 84107-45-9; **6d**, 84073-42-7; **7b**, 84064-73-3; **7c**, 84064-74-4; **7d**, 84064-75-5; *threo*-1-(3-methoxy-4-hydroxyphenyl)-1-(9-hydroxyanthacen-10-yl)-2-(2-methoxyphenoxy)propane, 84073-43-8.

Stereoselective Addition of Organocopper Reagents to a Novel Carbohydrate-Derived 2,3-Dihydro-4*H*-pyran-4-one[1]

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Stereoselective organocopper additions to a novel carbohydrate-derived 2,3-dihydro-4*H*-pyran-4-one are described. Stereochemical orientations are ascertained by scrutiny of high-resolution ^{1}H NMR spectra of these adducts as well as enol acetates derived therefrom.

The development of a convergent synthesis of maytansinoids[2] led to the need for tetrahydro-4*H*-pyran-4-ones of general structure **1** with the indicated absolute configuration. Concordant with this objective, a stereoselective conjugate addition of organocopper reagents to a novel 2,3-dihydro-4*H*-pyran-4-one has been crafted, and the product stereochemistry has been revealed by high-resolution ^{1}H NMR spectroscopy.

2,3-Dihydro-4*H*-pyran-4-one Synthesis

A few 2,3-dihydro-4*H*-pyran-4-ones have been previously prepared from D-glucal (**2**).[3,4] The present synthesis de-

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