Acetyl-7-oxotaxol (150 mg) was dissolved in CH_2Cl_2 (0.5 mL) containing 0.5% DBU. Reaction occurred immediately, and workup by standard methods gave the secotaxol **13** (143 mg, 95%): FABMS, m/z 916 (MNa^+) 894 (MH^+), 876 ($MH^+ - H_2O$), 834 (MH^+ - AcOH), 549 (MH^+ - RCOOH - H_2O), 507 (MH^+ - RCOOH - AcOH); m/z 894.3236 (MH^+; $C_{49}H_{53}NO_{15}$ requires 894.3338); IR 1760, 1745, 1675, 1530, 1505, 1470, 1390, 1280, 1240, 1105, 1085, 1075, 720, cm^{-1}; ^1H NMR, see Table I. $[\alpha]^{21}_D$ - 77.2° (c 0.004 MeOH).

7-Oxo-5,6-dehydro-5,*O*-secotaxol (14). Taxol (50 mg) in acetone (0.5 mL) was treated with Jones' reagent (0.02 mL) at room temperature and the mixture allowed to stand for 20 min. Standard workup gave 7-oxotaxol (**6**), which was purified by preparative TLC with elution by ethyl acetate–hexane (1:1). Opening of the oxetane ring occurred on the TLC plate, and 7-oxo-5,6-dehydro-5,*O*-secotaxol (**14**) was isolated (35 mg, 70%): FABMS, m/z 890 (MK^+), 874 (MH^+), 834 ($MH^+ - H_2O$), 549 (MH^+ - RCOOH - H_2O), 507 (MH^+ - RCOOH - AcOH); IR 1765, 1745, 1685, 1695, 1530, 1505, 1470, 1380, 1265, 1230, 1100, 1075, 1045 cm^{-1}; ^1H NMR, see Table I.

Reaction of 2′-Acetyl-7-oxotaxol with Borohydride. 2′-Acetyl-7-oxotaxol (**5**; 14 mg) and tetrabutylammonium borohydride (6 mg) were dissolved in dry CH_2Cl_2 (0.3 mL) and the mixture stirred at room temperature. All the starting material had disappeared after 8 min, reaction was stopped by adding several drops of acetone, and the mixture was worked up by standard methods. Analysis by ^1H NMR and TLC showed the major product to be 2′-acetyl-7-oxo-5,6-dehydro-5,*O*-secotaxol (**13**), with no evidence of reduction of either carbonyl group or the double bond.

Hydrogenation of 13 with Palladium Catalyst. A sample of 2′-acetyl-7-oxo-5,6-dehydro-5,*O*-secotaxol (**13**; 10 mg) was hydrogenated in ethyl acetate over 5% palladium on carbon (4 mg). No reaction was detected by TLC over a period of 12 h.

Hydrogenation of 7-Oxo-5,6-dehydro-5,*O*-secotaxol with Platinum Catalyst. 7-Oxo-5,6-dehydro-5,*O*-secotaxol (**14**; 35 mg) and 5% platinum on carbon (17 mg) in methanol (10 mL) was hydrogenated at room temperature for 3 h, at which point HPLC analysis showed the absence of starting material. The catalyst was filtered off, the methanol evaporated, and the lactone product **17** isolated by preparative HPLC: yield, 27 mg (77%); FABMS, m/z 876 (MNa^+), 854 (MH^+), 509 (MH^+ - RCOOH - AcOH), 286 ($RCOOH^+$); m/z 854.3246 (MH^+; $C_{47}H_{52}NO_{14}$ requires 854.3389); IR 1800, 1765, 1753, 1740, 1690, 1667, 1643 cm^{-1}; ^1H NMR, see Table I; $[\alpha]^{21}_D$ - 38.6° (c 0.002, MeOH).

2′-Acetyl-7-oxo-5,*O*-secotaxol (16). 2′-Acetyl-7-oxo-5,6-dehydro-5,*O*-secotaxol (**13**; 39 mg) and 5% platinum on carbon (23 mg) in ethyl acetate (5 mL) was hydrogenated for 3 h at room temperature. The catalyst was filtered off and the solvent removed on a rotary evaporator at 30 °C, followed by drying in a vacuum desiccator for several hours. ^1H NMR of the crude product showed the presence of two compounds, but on standing in $CDCl_3$ for 24 h only the major product **16** could be detected by ^1H NMR, together with minor impurities estimated at 10% or less of the mixture. Compound **16** was obtained as an unstable substance: FABMS m/z 551 (MH^+ - RCOOH - H_2O), 509 (MH^+ - RCOOH - AcOH), 328 ($RCOOH_2^+$), 268 ($RCOOH^+$ - AcOH), 105; IR 1745, 1720, 1675, 1530, 1500, 1470, 1385, 1280, 1240, 1105, 1085, 1050 cm^{-1}; ^1H NMR, see Table I.

Acknowledgment. We thank Dr. F. Boettner (Polysscience, Inc.) and Dr. M. Suffness (National Cancer Institute) for gifts of partially purified taxol fractions and of pure taxol, respectively. We acknowledge the assistance of the staffs of the Midwest Center for Mass Spectrometry and the Middle Atlantic Mass Spectrometry Laboratory, for mass spectral determinations. Financial support from the American Cancer Society (Grant CH-268) is gratefully acknowledged.

Transannular Acetal Synthesis: Studies Related to the Synthesis of Oxide-Bridged Terpenes

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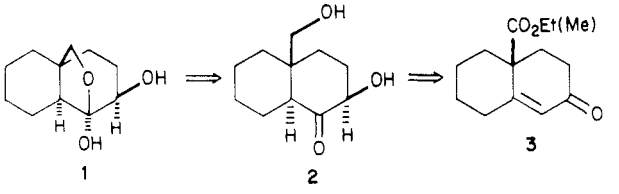
Synthesis of a transannular acetal model for oxide-bridged terpenoid systems was investigated. The use of Lewis acid catalyzed epoxide opening/rearrangement to generate the desired keto diol **2** was unsuccessful. However, Brönsted acid catalyzed intramolecular cyclization between a hydroxyl group and an enol ether gave the acetal **13** which could be hydrolyzed to the target hemiacetal **1**.

Several very challenging synthetic targets possess acetals and hemiacetals as key structural features.[2] The exploration of possible synthetic methods for the preparation of bridged hemiacetals and the reactivity of these units was of interest to us. Disclosed herein is a strategy for formation of this functional group, along with some stereochemical and chemical aspects of this naturally occurring unit.

Scheme I



The basic source of our model is illustrated in Scheme I.

It was reasoned that if *trans*-keto diol **2** was formed, it would close to the desired model, hemiacetal **1**. In turn, diol **2** would seem readily accessible from ester **3**.[3] Se-

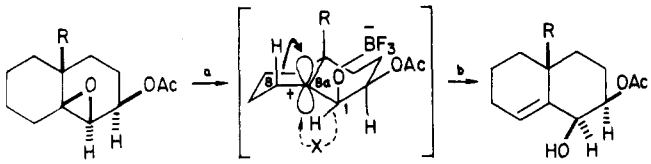
(1) To whom all correspondence should be addressed.

(2) The terms ketal and hemiketal have been abandoned in favor of the terms acetal and hemiacetal (IUPAC. "Nomenclature of Organic Chemistry"; Pergamon Press: New York, 1979; Section C, Rule 331.1). Quassinoids: Polonsky, J. *Fortschr. Chem. Org. Naturst.* **1973**, *30*, 101. Botryodiplodin: Moreau, S.; Lablanche-Combier, A.; Biguet, J.; Foulon, C.; Delfosse, M. *J. Org. Chem.* **1982**, *47*, 2358. 2-Desoxylemnacarnol: Izac, R. R.; Schneider, P.; Swain, M.; Fenical, W. *Tetrahedron Lett.* **1982**, *3*, 817. Palytoxin: More, R. E.; Bartolini, G. *J. Am. Chem. Soc.* **1981**, *103*, 2491. Lineatin: Slessor, K. N.; Oehlschlager, A. C.; Johnston, B. D.; Pierce, H. C., Jr.; Grewal, S. K.; Wichremesinghe, L. K. G. *J. Org. Chem.* **1980**, *45*, 2290. Humistratin: Nishio, S.; Blum, M. S.; Silverton, J. V.; Highet, R. J. *Ibid.* **1982**, *47*, 2154. α-Multistriatin: Sherk, A. E.; Fraser-Reid, B. *Ibid.* **1982**, *47*, 941.

(3) Marshall, J. A.; Greene, A. E. *J. Org. Chem.* **1971**, *36*, 2035 and references cited therein.

0022-3263/86/1951-0802$01.50/0

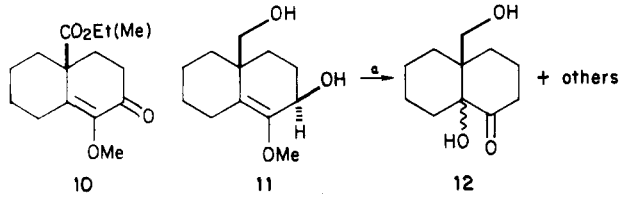
Scheme II[a]



7, R = CO_2Me (or CH_2OAc) 8 9, R = CO_2Me (or CH_2OAc)

[a] a, $BF_3 \cdot Et_2O/CH_2Cl_2/0$ °C; b, H_2O.

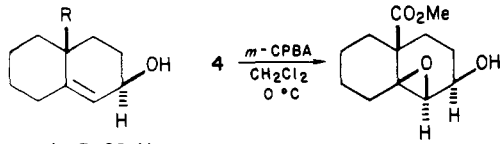
Scheme III[a]



10 11 12

[a] a, 10% HCl(aqueous)acetone.

lective[4] and complete hydride reduction of ester **3** led to ester alcohol **4** and diol **5**, respectively. Directed ep-



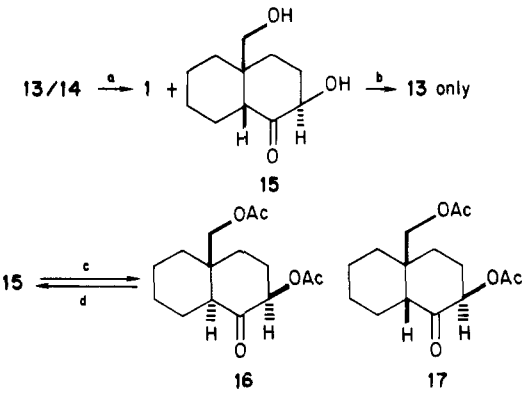
4, R = CO_2Me
5, R = CH_2OH **6**

oxidation[5] with *m*-chloroperbenzoic acid (*m*-CPBA) was only achieved on ester alcohol **4** to yield epoxide **6**. Attempted rearrangement of **6** under Lewis acid conditions gave the starting enone **3** presumably by Lewis acid coordination with the more basic hydroxyl moiety and concomitant 1,2 hydride shift of the hydroxyl methine.

Further, reactions with epoxide **7** gave, among other products, allylic alcohol **9** as the predominant product presumably arising from the tertiary carbonium ion intermediate **8** (see Scheme II). The α-oriented hydrogen on C-1, after formation of the carbonium ion at C-8a, is situated in a plane orthogonal to the node of the empty p orbital of the carbocation. Hence, the anticipated 1,2 hydride shift cannot occur readily. However, the axial proton at C-8, being in an antiperiplanar orientation, is ideally suited to irreversible elimination to give alcohol **9** after hydrolysis.

Because this epoxide showed a propensity to rearrangement in an undesired manner, we were led to construct the vinyl ether **10**.[6] Reduction of **10** with $LiAlH_4$ gave the diol **11** which upon treatment with aqueous acid gave predominantly a keto diol **12**. No evidence of the formation of hemiacetal **1** or keto diol **2** was obtained. The formation of **12** from **11** seems to involve rearrangements somewhat analogous to those described above (see Scheme III).

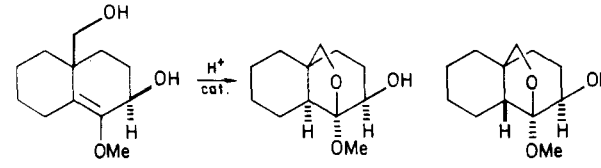
Scheme IV[a]



15 **16** **17**

[a] (a) 20% H_2SO_4(aqueous)/THF; (b) MeOH/concentrated HCl; (c) Ac_2O/pyr/DMAP/Et_2O; (d) K_2CO_3/MeOH.

However, intramolecular cyclization of diol vinyl ether **11** to give a transannular acetal could be achieved quantitatively under a variety of nonaqueous acid catalyzed conditions. Conditions such as ethereal chloroform solution exposed to light for several days and chloroform alone exposed to light for 10–12 hours provided *trans*-acetal **13**/*cis*-acetal **14** as 20:1 and 1:1 mixtures, respectively. The cyclization process presumably involves light-induced HCl generation in situ since exclusion of light totally suppressed the reaction. Use of dry HCl in benzene produced *trans*-acetal **13**/*cis*-acetal **14** (1:1) quantitatively within 2 min of treatment. Reaction of vinyl ether **11** in PTS/$CHCl_3$ for several hours also yielded 20:1 mixtures of *trans*-acetal **13**/*cis*-acetal **14** although contaminated with



11 **13** **14**

unassignable byproducts. The stereochemical assignments of **13** and **14** were based on ^{13}C NMR,[13] ^1H NMR lanthanide ($Eu(fod)_3$) induced shift correlations,[14] and two dimensional NMR.[15]

Complete isomerization of crystalline *cis*-acetal **14** to *trans*-acetal **13** could be effected in a media of silica gel and methylene chloride containing a trace of 20% aqueous sulfuric acid.

The predominance of the trans system under conditions more conducive to proton transfer suggests that the cis system may be the kinetic cyclization product and the trans the thermodynamic. The Allinger MM2 algorithm program[12] and even Dreiding models suggest that the *trans*-acetal should be more stable than the *cis*-acetal but,

(4) Moss, R. E.; Chen, E. Y.; Banger, J.; Matsuo, M. *Tetrahedron Lett.* **1978**, 4365.

(5) Henbest, H. B. *Proc. Chem. Soc. London* **1963**, 159. House, H. O. "Modern Synthetic Reactions", 2nd Ed; Benjamin Cummins: Menlo Park, CA, 1972; pp 292–317 and references cited therein.

(6) For preparation of 1,4-dimethoxybutan-2-one as an α-diketone carbanion synthon for annulation, see: Hennion, G. F.; Kupiecki, F. P. *J. Org. Chem.* **1953**, *18*, 1601. Caine, D.; Tuller, F. N. *Ibid* **1969**, *34*, 222.

(7) Commercially available from Aldrich Chemical Co., Milwaukee, WI—contains about 40% methyl ester.

(8) The dilute nature of the reaction mixture was envisioned to aid in product isolation by minimizing unwanted side reactions.

(9) Late eluting fractions during chromatography were shown by ^1H NMR to contain enone **10** possessing an ethyl ester exclusively.

(10) This material was allowed to stand in a closed clear glass container for at least 24 h prior to use.

(11) Chromatography on this material causes 30–40% loss of material with no apparent improvement in quality. The neat material appears relatively stable; in solution, appreciable decomposition occurred within 48 h.

(12) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 2.

(13) The stereochemical conformatory ^{13}C NMR assignments for **13** and **14** were made by analogy to bridgehead methyl *cis*- and *trans*-decalins.

(14) Incremental addition of $Eu(fod)_3$ to pure **13**, and **14** contaminated with **13** supports the stereochemical assignments; LSR experiments were performed according to: Willcott, M. R., III; David, R. E.; Holden, R. W. *J. Org. Chem.* **1975**, *40*, 1952.

(15) High-field two-dimensional NMR spectra of **13** and **14** were obtained through the NSF Regional Nuclear Magnetic Resonance Laboratory at the University of South Carolina and will be published elsewhere.

as of the present, direct evidence for the mechanistic source of **13** and **14** is not available.

Hydrolysis of the acetal **13** under strongly acidic conditions yields the desired *trans* hemiacetal **1**. A mixture of acetals **13** and **14** when hydrolyzed afforded **1** and opened *cis*-keto diol **15**. Reaction of **1** and **15** with acetic anhydride and pyridine yielded epimeric decalins **16** and **17**, respectively (see Scheme IV). Methanolic K_2CO_3 reforms a mixture of **1** and **15** with some apparent epimerization of the cis system to trans during the acylation–deacylation sequence of reactions. Significant is the fact that the cis system does not undergo cyclization to *cis* hemiacetal **1** as does the trans system. Finally, we observed that a mixture of hemiacetal **1** and keto diol **15** will reform the *trans*-acetal **13** exclusively on treatment with methanolic HCl.

The extensive rearrangements that were observed in these systems and the surprising ease of formation of the target model system **1**, has encouraged us to undertake additional studies within this series of compounds.

Experimental Section

(2α,4aα)-Octahydro-4a-(methoxycarbonyl)naphthalen-2-ol (4). Enone **3** (4.87 g, 23.4 mmol) was dissolved in ether and added to a stirred solution of lithium tri-*tert*-butoxyaluminum hydride (7.14 g, 28.1 mmol) in ether. The mixture was refluxed for 3 h and stirred at room temperature overnight. Sequential addition of water, 15% aqueous sodium hydroxide, and water gave a gummy suspension. This mixture was diluted with ether and washed with water and saturated brine solution. The ethereal layer was dried over magnesium sulfate. Filtration of inorganic salts and solvent removal under reduced pressure afforded 4.3 g of yellow oil. Chromatography using a Waters Prep 500/A LC system with ether/cyclohexane, 2:1 (v/v), as eluant gave 3.11 of clear oil (allylic alcohol **4**, 64%): TLC (silica gel; ether), R_f 0.36; IR (film; cm^{-1}) 3410, 2925, 2860, 1720, 1660, 1445, 1430; ^1H NMR (ppm) 5.45 (br s, 1 H, vinyl), 4.03 (dstr t, 1 H, allylic methine), 3.66 (s, 3 H, C*H*$_3$ ester); ^{13}C NMR (ppm) 175.91 (C=O ester), 135.43 (C-8a), 126.65 (C-1), 66.35 (C-2), 51.48 (CH_3 ester), 47.92 (C-4a), 37.94 (C-4), 33.39 (C-3), 33.33 (C-8), 28.47 (C-5), 27.01 (C-6), 23.37 (C-7); MS (210 (7, M^+), 192 (12, $M^+ - H_2O$), 179 (12, $M^+ - OCH_3$), 151 (50, M^+ – COOMe), 133 (75, M^+ – COOMe – H_2O), 91 (100, B, M^+ – COOMe – H_2O – C_3H_6).

(1α,2α,4aα,8aα)-Octahydro-4a-(methoxycarbonyl)-1,8a-epoxynaphthalen-2-ol (6). To a stirred solution of *m*-chloroperbenzoic acid (99 + %; 3.07 g, 17.8 mmol) in methylene chloride at 0 °C was added allylic alcohol **4** (3.11 g, 14.8 mmol) in methylene chloride. The mixture stirred overnight at 0 °C. While being kept at 0 °C, the solution was vacuum filtered. The organic solution was then washed with saturated sodium sulfite solution, saturated sodium bicarbonate solution, water, and saturated brine. Drying the solution over magnesium sulfate and then filtering and concentration in vacuo furnished an opaque yellow oil, which was filtered through a short column of Florisil (60–200 mesh) using ether as eluant. Evaporation under reduced pressure gave 2.74 g of yellow oil (hydroxy epoxide **6**, 83%) which was sufficiently pure for further use: TLC (silica gel; ether) R_f 0.23; IR (film; cm^{-1}) 3440, 2925, 2850, 1715, 1440, 1195; ^1H NMR (ppm) 3.93 (br q, J = 4 Hz, –C*H*OH), 3.7 (s, 3 H, CH_3 ester), 2.9 (d, J = 4 Hz, 1 H, epoxy methine).

(1α,2α,4aα)-Octahydro-2-acetoxy-4a-(methoxycarbonyl)-naphthalen-1-ol (9). Boron trifluoride etherate complex (BF_3·Et_2O, 400 mg, 2.8 mmol) was added in one portion to a stirring solution of epoxy acetate **7** (685 mg, 2.6 mmol) in methylene chloride (45 mL)[8] at 0 °C. The disappearance of starting material was monitored by TLC. At intervals of 15 min and 80 min, BF_3-Et_2O (170 mg and 400 mg) was added, respectively. After 95 min, the mixture was quenched by the addition of saturated sodium bicarbonate solution. The organic phase was washed with brine and dried over magnesium sulfate. Filtration and concentration to dryness furnished 710 mg of a viscous orange oil which upon treatment with ether gave 370 mg (54%) of fine white crystals (allylic alcohol **9**): mp 134.5–135.5 °C; TLC (silica gel; ether) R_f 0.32; IR ($CHCl_3$; cm^{-1}) 3615, 3450, 2020, 2840, 1720, 1660, 1450, 1370, 1240; ^1H NMR (ppm) 6.03 (br t, J = 4 Hz and 4 Hz, 1 H, vinyl), 4.72 (dq, J = 11, 5, and 3 Hz, 1 H, –CHOAc), 4.33 (dstr d, J = 3 Hz, 1 H, allylic methine), 3.73 (s, 3 H, CH_3 ester), 2.1 (s, 3 H, CH_3 acetate); ^{13}C NMR (ppm) 178.10 (C=O ester), 170.34 (C=O acetate), 135.13 (C-8), 132.01 (C-8a), 74.96 (C-2), 73.98 (C-1), 52.37 (CH_3 ester), 45.48 (C-4a), 35.45 (C-4), 34.5 (C-3), 24.97 (C-7), 22.47 (C-5), 21.17 (C-6), 18.94 (CH_3 acetate); MS 268 (0.1, M^+), 208 (10, M^+ – COOMe – H), 149 (55, M^+ – 2 (COOMe – H), 43 (100, B); (15 eV) 268 (1), 251 (1, M^+ – OH), 208 (36), 149 (100, B). Anal. Calcd for $C_{14}H_{20}O_5$ (M_r 268.13): C, 62.66; H, 7.52. Found: C, 62.56; H, 7.57.

4,4a,5,6,7,8-Hexahydro-1-methoxy-4a-(ethoxycarbonyl)-2-(3*H*)-naphthalenone (10). The following is a modified procedure of Marshall and Greene.[3] 1,4-Dimethoxy-2-butanone[6] (8.54 g, 64.7 mmol) in absolute ethanol was added over a 3-h period to a stirred solution of ethyl 2-oxo-cyclohexane-1-carboxylate[7] (11 g, ca. 64.7 mmol) in 0.08 M sodium ethoxide/ethanol cooled to –5 to –15 °C. Once addition was completed, 1 M NaOEt/EtOH was added and the mixture warmed to room temperature. After 14 h, 1 M NaOEt/EtOH was added followed by additional butanone. This mixture was allowed to stir for 3.5 h. Excess base was neutralized (as assayed by pH paper) with glacial acetic acid. The neutralized mixture was poured into water and extracted with methylene chloride. Combined organic layers were dried over magnesium sulfate and filtered. Evaporation of solvent in vacuo gave viscous orange oil. Silica gel chromatography (Waters Prep 500 A LC, 50% ether in hexane) afforded unreacted ethyl cyclohexanone-2-carboxylate (2.85 g) and 7.1 g (ca. 59%, based on recovered starting material) of pale yellow oil (enone **10**, 83% ethyl ester by proton NMR):[9] IR (film; cm^{-1}) 2920, 2850, 1710, 1675, 1625, 1435, 1160; ^1H NMR (ppm) 4.2 (q, J = 6 Hz, 2 H, C*H*$_2$ ester), 3.63 (s, 3 H, C*H*$_3$ enol ether), 1.3 (t, J = 6 Hz, C*H*$_3$ ester); ^{13}C NMR (ppm) 193.22 (C-2), 173.13 (C=O ester), 148.21 (C-1), 146.78 (C-8a), 60.91 (CH_2 ester), 59.52 (CH_3 enol ether), 48.68 (C-4a), 38.12 (C-4), 34.73 (C-3), 33.59 (C-5), 25.31 (C-8), 24.77 (C-6), 22.42 (C-7), 13.77 (CH_3 ester); GC/MS 252 (18, M^+), 179 (100, B, M^+ – COOEt), 151 (62, M^+ – COOEt – C_2H_4).

(2α,4aα)-Octahydro-1-methoxy-4a-(hydroxymethyl)-naphthalen-2-ol (11). To a solution of lithium aluminum hydride (260 mg, 6.9 mmol) and ether at 0 °C was slowly added enone ester **10** (1.45 g, ca. 5.7 mmol) in ether. After stirring for 25 min, Glauber's salt (Na_2SO_4·10 H_2O) was added in small increments until gas evolution had ceased. Filtration of the mixture and evaporation in vacuo left a pale yellow oil which was chromatographed (silica gel, 230–400 mesh; ethyl acetate as eluant) affording 938 mg (ca. 78%) of clear viscous oil (diol **11**) which solidified on standing: mp 79–82 °C. An analytical sample was obtained by recrystallization from ether, mp 81–82 °C: TLC (silica gel; ethyl acetate) R_f 0.26; (silica gel; ether) R_f 0.15; IR (film; cm^{-1}) 3360, 2940, 2860, 1660, 1445, 1115, 1020; ^1H NMR (ppm) 4.26 (t, J = 5 Hz, 1 H, allylic methine), 3.8, 3.43 (AB q, J_{AB} = 12 Hz, 2 H, C*H*$_2$OH), 3.6 (s, 3H, C*H*$_3$ enol ether); ^{13}C NMR (ppm) 150.17 (C-1), 124.95 (C-8a), 64.41 (CH_2OH), 64.31 (C-2), 57.99 (CH_3 enol ether), 39.89 (C-4a), 35.05 (C-4), 28.74 (C-3), 27.68 (C-5), 27.24 (C-8), 22.19 (C-7), 21.60 (C-6); MS 212 (5, M^+), 194 (2, $M^+ - H_2O$), 181 (91, $M^+ - CH_2OH$), 164 (23, $M^+ - CH_2OH - OH$), 153 (100, B, $M^+ - CH_2OH - C_2H_4$), 149 (93, $M^+ - CH_2OH - CH_3OH$); (15 eV) 212 (4, M^+), 181 (100, B), 164 (16), 153 (7), 149 (6). Anal. Calcd for $C_{12}H_{20}O_3$ (M_r 212.14): C, 67.89; H, 9.50. Found: C, 67.9; H, 9.55.

(1α,2α,4aα,8aβ)-Decahydro-1-methoxy-1,4a-(epoxymethano)naphthalen-2-ol (13). Diol **11** (500 mg, 2.36 mmol) was dissolved in 50% ether/chloroform solution[10] and allowed to stand for 60 h. Concentration in vacuo left 500 mg of pale yellow oil which contained 95% of *trans*-acetal **13** and the remainder as its isomer, *cis*-acetal **14**: TLC (silica gel; ether) R_f 0.25; IR (film; cm^{-1}) 3440, 2910, 2850, 1490, 1440, 1230, 1090; ^1H NMR (ppm) 4.13 (dd, J = 8 and 2 Hz, 1 H, –C*H*O–, H_S), 3.8 (dd, J = 6 and 9 Hz, 1 H, –C*H*OH), 3.46 (d, J = 8 Hz, 1 H, –C*H*O–, H_R, partially obscured by s at 3.43 (s, 3 H, CH_3 ether); (benzene-d_6) 3.89 (dd, J = 8 and 2 Hz, 1 H, –C*H*O–, H_S), 3.63 (dd, J = 6 and 9 Hz, 1 H, –C*H*OH), 3.4 (s, 3 H, C*H*$_3$ ether), 3.2 (d, J = 8 Hz, 1 H, –C*H*O–, H_R); ^{13}C NMR (ppm) 110.01 (C-1), 72.01 (C-2), 71.39 (–CH_2O), 52.52 (CH_3 ether), 42.11 (C-8a), 42.66 (C-4a), 37.52 (C-4), 30.1 (C-5), 29.01 (C-3), 24.17 (C-8), 21.7 (C-6), 21.61 (C-7); GC/MS

212 (3, M^+), 194 (3, $M^+ - H_2O$), 180 (2, $M^+ - CH_3OH$), 162 (8, $M^+ - CH_3OH - H_2O$), 153 (100, B, $M^+ - C_3H_7O$).

(1α,2α,4aα,8aα)-Decahydro-1-methoxy-1,4a-(epoxymethano)naphthalen-2-ol (14). A solution of diol **11** (100 mg, 0.5 mmol) in chloroform[10] was allowed to stand under ambient atmosphere for 9.5 h. Concentration under reduced pressure gave 100 mg of clear oil which contained ca. 1:1 mixture of *trans*-acetal **13** and *cis*-acetal **14**. Addition of hexane and 10 h at −30 °C afforded 39 mg (ca. 78%, based on available **14**) of white crystals (*cis*-acetal **14**): mp 101–102 °C. TLC and IR were identical with *trans*-acetal **13**: ^{1}H NMR (ppm) 3.83 (d, J = 8 Hz, 1 H, –C*H*O–, H_R), 3.73 (m, 1 H, –C*H*OH), 3.57 (dd, J = 8 and 2 Hz, 1 H, –C*H*O–, H_S), 3.33 (s, 3H, CH_3 ether); ^{13}C NMR (ppm) 107.66 (C-1), 78.48 (–CH_2O–), 69.16 (C-2), 48.72 (CH_3 ether), 44.57 (C-8a), 41.47 (C-4a), 33.49 (C-4), 27.98 (C-3), 25.83 (C-5), 25.73 (C-8), 20.85 (C-6), 19.91 (C-7); MS 212 (2, M^+), 194 (2, $M^+ - H_2O$), 181 (2, $M^+ - CH_3O$), 162 (14, $M^+ - CH_3OH - H_2O$), 153 (67, $M^+ - C_3H_7O$), 93 (100, B, $M^+ - C_3H_7O - C_2H_4O_2$); (16 eV) 212 ($M^+$), 194 (8), 180 (5), 181 (4), 162 (28), 153 (100, B). Anal. Calcd for $C_{12}H_{20}O_3$ (M_r 212.14): C, 67.89; H, 9.50. Found: C, 67.92; H, 9.55.

(1α,2α,4aα,8aβ)-Decahydro-1,4a-(epoxymethano)naphthalene-1,2-diol (1). To a mixture of acetal **13** (150 mg, 0.7 mmol) in tetrahydrofuran was added a solution of 20% aqueous sulfuric acid and tetrahydrofuran. The reaction mixture was allowed to stir at room temperature under ambient atmosphere for 1.5 h. Brine was added and the resulting mixture was washed with 50% ethyl acetate in ether. The organic washings were dried over potassium carbonate, filtered, and concentrated to afford 135 mg (96%) of pale yellow oil (hemiacetal **1**):[11] TLC (silica gel; ether) R_f 0.2; IR (film; cm^{-1}) 3400, 2920, 2840, 1450, 1230; ^{1}H NMR (ppm) 4.06 (br d, H = 8 Hz, 1 H, –CHO–), 3.6 (env, 1 H, –C*H*OH), 3.4 (d, J = 8 Hz, 1 H, –CHO–); ^{13}C NMR (ppm) 106.79 (C-1), 74.26 (C-2), 70.95 (–CH_2O), 48.3 (C-8a), 42.29 (C-4a), 37.72 (C-4), 29.96 (C-5), 29.02 (C-3), 24.04 (C-8), 21.57 (C-7), 20.93 (C-6); MS 198 (1, M^+), 180 (1, $M^+ - H_2O$), 167 (2, $M^+ - CH_2OH$), 149 (15, $M^+ - CH_2OH - H_2O$), 121 (100, B, $M^+ - H_2O - CH_2OH - CO$).

Hemiacetal 1/Keto Diol 15 Mixture. A sample of *trans*-acetal **13** and *cis*-acetal **14** (200 mg, 0.9 mmol, 1:1) was treated with 20% aqueous sulfuric acid and tetrahydrofuran in identical fashion with the preceding preparation of hemiacetal **1**. Pale yellow oil (184 mg, ca. 98%) was obtained. ^{13}C NMR revealed two compounds of approximately equal proportion. The two compounds were hemiacetal **1** and keto diol **15**. ^{13}C NMR data for **15** is listed below: ^{13}C NMR (ppm) 215.18 (C-1), 71.18 (C-2), 69.05 (–CH_2O–), 52.65 (C-8a), 41.59 (C-4a), 32.83 (C-4), 31.1 (C-3), 26.92 (C-5), 25.24 (C-8), 23.88 (C-6), 20.73 (C-7).

***trans*-(2α,4aα)-Octahydro-2-acetoxy-4a-(acetoxymethyl)-1(2*H*)-naphthalenone (16).** A solution of hemiacetal **1** (135 mg, 0.7 mmol), acetic anhydride (146 mg, 1.43 mmol), pyridine, ether, and a catalytic amount of 4-(*N*,*N*-dimethylamino)pyridine was allowed to stir at room temperature for 5.5 h. Ether was added and the mixture was washed exhaustively with saturated copper sulfate solution, water, and brine. The ethereal solution was dried over magnesium sulfate and filtered. Concentration in vacuo afforded 176 mg (92%) of pale yellow oil (keto diacetate **16**). An analytical sample was obtained by distillation via Kugelrohr apparatus which gave colorless oil: bp 76–82 °C/0.75 mm; TLC (silica gel; ether), R_f 0.5; IR (film; cm^{-1}) 2930, 2850, 1730–1715, 1450, 1365, 1035, 890; ^{1}H NMR (ppm) 5.22 (dstr dd, J = 12 and 8 Hz, 1 H, –CHOAc), 4.12, 3.93 (AB q, 2 H, J = 12 Hz, –CH_2OAc), 2.12, 2.0 (s, 6 H, CH_3 acetates); ^{13}C NMR (ppm) 203.45 (C-1), 170.01, 169.47 (C=O acetates), 75.4 (C-2), 61.39 (–CH_2OR), 53.96 (C-8a), 41.99 (C-4a), 34.56 (C-4), 33.93 (C-3), 27.85 (C-5), 24.43 (C-8), 20.34 (C-6), 20.22, 20.16 (CH_3 acetates), 19.46 (C-7); GC/MS 282 (0.1, M^+), 240 (12, $M^+ - CH_2CO$), 209 (1, $M^+ - CH_2OCOCH_3$), 167 (3, $M^+ - CH_2OCOCH_3 - CH_2CO$), 149 (7, $M^+ - CH_3COOCH_3 - OCOCH_3$), 139 (100, B, $M^+ - CH_2 - OCHCH_3 - CO - CH_2CO$). Anal. Calcd for $C_{15}H_{22}O_5$ (M_r 282.15): C, 63.8; H, 7.52. Found: C, 63.72; H, 7.9.

***cis*-(2α,4aα)-Octahydro-2-acetoxy-4a-(acetoxymethyl)-1-(2*H*)-naphthalenone (17).** A mixture of 20% aqueous sulfuric acid and tetrahydrofuran was added to *cis*-acetal **14** (39 mg, 0.18 mmol) and allowed to stir at room temperature for 1.25 h. Isolation of material was accomplished in identical fashion with preparation of hemiacetal **1**. A pale yellow oil was obtained and immediately treated with acetic anhydride (108 mg, 1.1 mmol), pyridine, and a catalytic amount of 4-(*N*,*N*-dimethylamino)-pyridine. The mixture was stirred overnight. Product was isolated in identical fashion with the preceding preparation. Yellow viscous oil was obtained (keto diacetate **17**, 42 mg, 81%). TLC and IR were identical with keto diacetate **16**: ^{1}H NMR (ppm) 5.43 (dd, J = 12 and 8 Hz, 1 H, –CHOAc), 3.95, 3.72 (ABq, J = 12 Hz, 2 H, –CH_2OAc), 2.1, 2.0 (s, 6 H, CH_3 acetates); ^{13}C NMR (ppm) 206.25 (C-1), 170.53, 169.93 (C=O acetates), 72.68 (C-2), 70.53 (–CH_2OR), 53.91 (C-8a), 39.81 (C-4a), 33.15 (C-4), 27.42 (C-3), 26.2 (C-5), 25.02 (C-8), 24.82 (C-6), 20.63 (CH_3 acetates and C-7); GC/MS no M^+ at 282, 240 (8, $M^+ - CH_2CO$), 209 (13, $M^+ - CH_2$–$OCOCH_3$), 167 (11, $M^+ - CH_2OCOCH_3 - CH_2CO$), 149 (36, $M^+ - CH_3COOCH_3 - OCOCH_3$), 43 (100, B).

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