NMR (25.14 MHz, D_2O) δ 84.44 (minor), 83.09 (major), 79.16 (major), 76.20 (minor), 74.52 (major), 68.25 (minor), 62.23 (major), 61.87 (minor), 60.74. Anal. Found: C, 40.51; H, 5.73. Calcd for $C_6H_{10}O_6$: C, 40.45; H, 5.66.

(3*S*,4*R*)-2-Methylene-3-hydroxy-4-[(trityloxy)methyl]-γ-butyrolactone (22). To a suspension of lactone **9** (152 mg, 1.05 mmol) in CH_2Cl_2 (1 mL) were added Et_3N (192 μL), trityl chloride (382 mg, 1.37 mmol), and (dimethylamino)pyridine (5 mg). The mixture was stirred overnight at 40 °C, then the solvent was evaporated, and the product was isolated by flash chromatography (55:45 *n*-hexane–AcOEt) (162 mg, 40%): (Found: C 77.64, H 5.80%; $C_{25}H_{22}O_4$ requires: C 77.70, H 5.74%). IR ν_{max} 3600, 1765, 1600 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3/D_2O$) δ 3.43 (2 H, AB part of ABX system, J_{AB} = 6.4 Hz, J_{BX} = 3.6 Hz, J_{AX} = 3.6 Hz, CH_2OTry), 4.39 (1 H, X part of ABX system, $J_{AX} = J_{BX} = J_{XY}$ = 3.6 Hz, 4-H), 4.80 (1 H, m, 3-H), 5.99 (1 H, d, J = 2.0 Hz, trans HC=CCO), 6.51 (1 H, d, J = 2.0 Hz, cis HC=CCO), 7.23–7.50 (15 H, m, Ar).

Osmylation of 22. Lactone **22** was osmylated as described for the synthesis of **25**. Reaction products were isolated by flash chromatography (85:15 AcOEt–*n*-hexane) in 80% yield and subsequently detritylated with CF_3COOH to give a 8:1 mixture of lactones **23** and **24** (ratio determined by 200-MHz ^1H NMR).

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Synthesis of Hydrophenanthrene Natural Products: A Novel Approach. 1. Stereoselective Synthesis of Resin Acid Synthons†,‡

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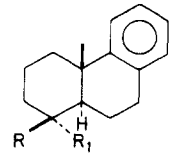
We report the conversion of 4a-methyl-2,4a,9,10-tetrahydrophenanthrene, (**8**), readily available from phenanthrene by reductive alkylation, via 4a-methyl-3,4,4a,9,10,10a-hexahydro-1(2*H*)-phenanthrone, (**5**), into both C-1 isomers of 1,4aβ-dimethyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene-1-carboxylic acid (**1a** and **1b**) by an efficient and stereoselective route. This is a new route to diterpenoid acids of the podocarpate and abietate families.

Numerous syntheses of resin acids and of structurally related compounds, both naturally occurring and synthetic, have been reported.[1] These include group **1a** structures with the abietic acid stereochemistry as well as group **1b** structures with podocarpic acid stereochemistry.

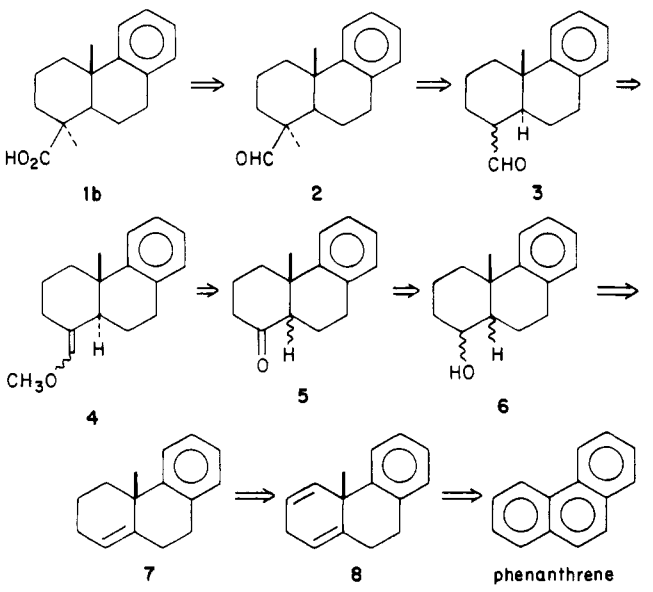


1a, R = CH_3; R_1 = CO_2H
1b, R = CO_2H; R_1 = CH_3

Unlike most efforts wherein efficient syntheses of specific natural products are the objective, we set as our goal the development of an efficient stereoselective total synthesis of both C-1 epimers, (±)-deoxypodocarpic acid and (±)-deisopropyldehydroabietic acid, from a common intermediate late in the synthetic sequence.

In the case of deoxypodocarpic acid, there is ample precedent that the correct stereochemistry can be established selectively by base-catalyzed alkylation of a 1-carboxaldehyde, presumably because the relatively bulky 4aβ-methyl group directs alkylation to the opposite (α) face of the molecule (Scheme I). There is adequate precedent for the preparation of octahydrophenanthrene-1-carboxaldehydes from the corresponding octahydro-1(2*H*)-phenanthrone via a Wittig homologation reaction. In addition to the homologation, Wittig reactions run under equilibrating conditions (i.e., sodium dimsyl in dimethyl sulfoxide) are known to establish stereoselectively the AB

Scheme I



trans stereochemistry.[1f] The 1(2*H*)-hydrophenanthrone, in turn, would be the expected product from an oxidation of the corresponding 1-hydrophenanthrol which has been prepared in three steps from phenanthrene by a reductive

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‡ Taken in part from the dissertation presented by T.N.T. to the Graduate School of the University of Kansas (1980) in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(1) (a) Cf. The series, "Terpenoids and Steroids", Specialist Periodical Reports, The Royal Society of Chemistry, Burlington House, London, WIV OBN, 1978. (b) Ireland, R. E.; Kierstead, R. C. *J. Org. Chem.* **1966**, *31*, 2543. (c) Sone, T.; Terashima, S.; Yamada, S. *Chem. Pharm. Bull.* **1976**, *24*, 1288. (d) Wenkert, E.; Tahara, A. *J. Am. Chem. Soc.* **1960**, *82*, 3229. (e) Meyer, W. L.; Sigel, C. W. *J. Org. Chem.* **1977**, *42*, 2769. (f) Ziegler, F. E.; Kloek, J. A. *Tetrahedron* **1977**, *33*, 373. (g) Trost, B. M.; Preckel, M. *J. Am. Chem. Soc.* **1973**, *95*, 7862. (h) Mathew, C. T.; Banerjee, G. C.; Dutta, P. C. *J. Org. Chem.* **1965**, *30*, 2754. (i) Wenkert, E.; Afonso, A.; Bredenberg, J. B.-s.; Kaneko, C.; Tahara, A. *J. Am. Chem. Soc.* **1964**, *86*, 2038. (j) Welch, S. C.; Hagan, C. P.; Kim, J. H.; Chu, P. S. *J. Org. Chem.* **1977**, *42*, 2879. (k) Barltrop, J. A.; Day, A. C. *Tetrahedron* **1961**, *14*, 310.

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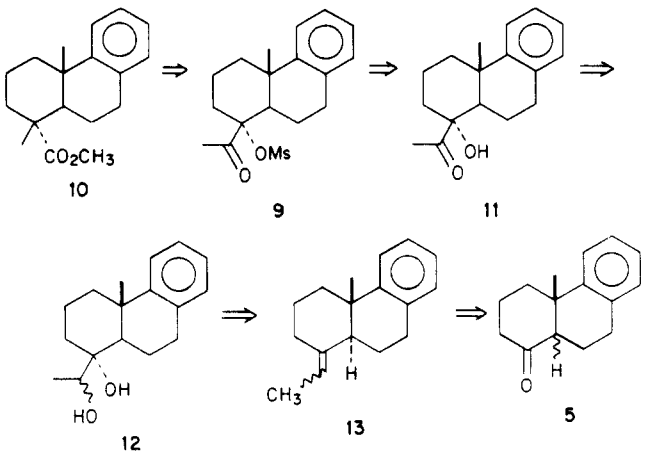
Scheme II



10 9 11 12 13 5

alkylation, selective partial hydrogenation, hydroboration–oxidation sequence.[2]

The abietic acid stereochemistry, however, is less easily obtained. An attractive route to the geminal methyl, carboxylate functionality seemed to be the Favorskii rearrangement of 1-acetylhydrophenanthrene appropriately substituted with a leaving group at C-1. Such ketones have been converted into geminal methyl carboxylates, and in some cases the reaction was stereoselective.[3]

An appropriate exocyclic olefin with the pro-acetyl methyl group already in place would likely yield a diol upon treatment with osmium tetraoxide. Steric factors would probably not prevent reaction in this case because both of the oxygens would be added simultaneously to a flat, relatively unhindered olefin. Moreover, addition from the α-face of the olefin might well be the favored approach because of steric hindrance to the β-face by the 4a-methyl group. Were this the case, the tertiary hydroxyl would have the α-orientation. The secondary hydroxyl of 1,2-diols with both secondary and tertiary hydroxy groups can be selectively oxidized to form hydroxy ketones. If such a hydroxy ketone could be mesylated, the Favorskii precursor would be in hand (Scheme II).

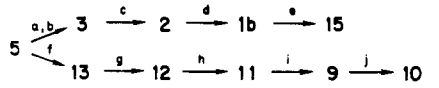
The synthetic route proposed is novel in two respects. First, the tricyclic ring system is intact from the start, an approach which no other group has taken in resin acid synthesis. Second, it should allow a stereoselective total synthesis of *both* C-1 epimers from a common intermediate *late* in the synthetic scheme.

Results and Discussion

With the strategy thus established, we set about reducing it to practice. The ketone **5**, as a mixture of isomers, was prepared from phenanthrene as described by Sierra et al.[2] Accordingly, the Wittig reaction of **5** with (methoxymethyl)triphenylphosphonium chloride in dimethyl sulfoxide and sodium hydride produced a mixture which, after acid hydrolysis and chromatography, afforded aldehyde **3** in 73% overall yield. This aldehyde was assigned the 1α stereochemistry on the basis of chemical shift comparisons to that of Ziegler and Kloek[1f] for a closely related compound. The ^{1}H NMR spectrum also clearly showed that **3** was a single ring-juncture isomer (Scheme III).

Aldehyde **3**, when treated with methyl iodide and 2.5 equiv of potassium *tert*-butoxide in *tert*-butyl alcohol and benzene, gave in 90% yield, a product, **2**, whose ^{1}H NMR

Scheme III[a]

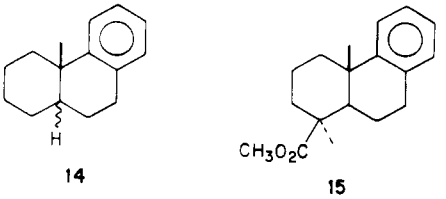


[a] (a) $Ph_3P^+CH_3Br^-$/NaH/Me_2SO/; (b) HCl/THF; (c) KO-*t*-Bu/*t*-BuOH/CH_3I; (d) CrO_3/H_2SO_4/acetone; (e) CH_2N_2/ether; (f) $Ph_3P^+CH_2CH_3Br^-$/NaH/Me_2SO; (g) OsO_4/pyr; (h) ClCOCOCl/Me_2SO/Et_3N; (i) MsCl/pyr; (j) $NaOCH_3$/DME.

signals for the two methyls and aldehyde proton corresponded to those of deoxypodocarpic aldehyde.[4] Without further purification, aldehyde **2** was oxidized with Jones reagent to produce a crystalline acid whose melting point[1i] and spectral data[4] corresponded to those of deoxypodocarpic acid. The acid was dissolved in ether and treated with diazomethane to afford a methyl ester whose IR, ^{1}H NMR, and melting point data were in agreement with those reported for methyl deoxypodocarpate.[4]

Attention was now turned to the elaboration of the abietic series. Olefin **13** was prepared from ketone **5** and ethyltriphenylphosphonium bromide in 70% yield after chromatography. Again, ^{1}H NMR indicated a single ring-junction isomer, presumably the 10a-αH isomer. Diol **12** was obtained by osmium tetraoxide oxidation of **13**. Neither Fetizon[5] or Jones oxidation of **12** produced the desired hydroxy ketone **11** cleanly. However, use of Omura and Swern[6] conditions produced **11** in 80–85% yield; the unreacted diol being readily recovered by chromatography. Conversion of **11** to mesylate **9** was accomplished with methanesulfonyl chloride in pyridine at 0 °C.

With mesylate **9** in hand, the stage was set for the critical Favorskii rearrangement. Accordingly, mesyl ketone **9** was dissolved in dimethoxyethane and allowed to react with 4 equiv of sodium methoxide.[3] Upon workup, a neutral material was isolated which showed the presence of three components by GC analysis in a 1:8:1 ratio. GC/MS analysis showed that the first and second peaks had molecular ions of m/z 272 as would be expected for either methyl deoxypodocarpate, **15**, or methyl deisopropyldehydroabietate, **10**. Coinjection of **15** showed that the minor isomer, eluting first, was methyl deoxypodocarpate. The major isomer, isolated by preparative TLC, had spectral data and melting point in close agreement with those of deisopropyldehydroabietic acid.[1i,4]



14 15

Successful stereoselective synthesis of both C-ring aromatic hydrophenanthrene-related resin acid groups, C-1 axial and C-1 equatorial carboxyl epimers, is thus completed. As this is accomplished from a common intermediate well along the synthetic route, the means for preparation of many related natural products are in hand. Further, as this common intermediate is available in only four steps (all of which can be carried out in sequence without purification of intermediates) from phenanthrene, this synthesis route is highly efficient and amenable to large-scale preparations.

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(5) Bastard, J.; Fetizon, M.; Gramain, J. C. *Tetrahedron* **1973**, *29*, 2867.
(6) Omura, K.; Swern, D. *Tetrahedron* **1978**, *34*, 1651.

Experimental Section

All melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were obtained with a Beckman IR-33, Perkin-Elmer 257, or Perkin-Elmer 281B spectrometer in a 2% $CHCl_3$ solution, as a 1% KBr pellet or as a thin film between NaCl plates. ^1H NMR spectra were obtained with a Varian EM-360 or a JEOL C-60HL spectrometer. FT ^1H NMR spectra and ^{13}C NMR spectra were obtained with a JEOL FX60 spectrometer. All NMR spectra were obtained in a $CDCl_3$ solution unless otherwise indicated and are reported in δ units (ppm) relative to tetramethylsilane (Me_4Si). Mass spectra were recorded with a Varian Associates CH-5 mass spectrometer, a DuPont Model 21-492 GC/MS, a Hewlett-Packard 5985 GC/MS/DS, or a Finnigan 3200 F GC/MS/DS. Microanalyses were performed on a Hewlett-Packard 185B CHN analyzer, Department of Medicinal Chemistry, University of Kansas. Gas chromatographic analyses (GC) were obtained with a Varian Associates Model 3700 (10 ft × $^1/_8$ in 6% SE-30 on Chromasorb W, 100 mesh) or a Perkin-Elmer 900 (6 ft × $^1/_8$ in. 3% Carbowax 20M on Chromasorb W 100/120-mesh DMCS-AW, or 6 ft × $^1/_8$ in. 3% OV-17 on Chromasorb W 100/120 mesh) chromatograph equipped with a flame ionization detector with helium or nitrogen as the carrier gas at a flow rate of ca. 30 mL/min. Quantitative GC analyses were made by using the method of internal standards as described by McNair and Bonelli.[7] Liquid chromatography was performed with Brinkman silica gel 60 (70–235 mesh). Preparative and thin-layer chromatography (TLC) were performed on Brinkman precoated plates. Preparative scale pressure-assisted liquid chromatography was performed with Merck silica gel 60 (230–400 mesh) at ca. 70 psi on 1 m × 2 cm glass columns and a solvent flow rate of 20 mL/min.

Solvents used for chromatography were distilled prior to use. Ether, tetrahydrofuran (THF), and dimethoxyethane (DME) used as cosolvents in the reductive alkylations were distilled from lithium aluminum hydride (LAH) immediately prior to use. Dimethyl sulfoxide (Me_2SO) was dried by stirring over CaH at 70 °C overnight followed by distillation at reduced pressure. All other solvents used were of analytical reagent grade or purified according to literature methods.

All reactions using dry solvents were run in flame-dried apparatus under a positive pressure of argon. All transfers of reagents were made under anhydrous conditions with a syringe or cannula. Usual workup of a reaction involved extraction with a solvent, a wash with saturated NaCl solution (brine), drying with anhydrous granular $MgSO_4$, Na_2SO_4, or K_2CO_3, and concentration in vacuo (rotary evaporator).

4aβ-Methyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene-1-carboxaldehyde (3). The method of Ziegler and Kloek[1f] was used. Dimsylsodium was generated in situ as described from 50% NaH dispersion (1.66 g, 33.7 mM) and Me_2SO (40 mL). This was cooled to 25 °C and a solution of (methoxymethyl)triphenylphosphonium chloride (21.6 g, 36.7 mM) in dry Me_2SO (40 mL) was added. The resultant red solution was stirred 5 min before addition of ketone **5** (2.65 g, 12.4 mM) in dry Me_2SO (30 mL). The reaction mixture was stirred under argon at 25 °C until TLC (benzene/hexane, 7:3) showed no ketone remaining (ca. 6 h). The reaction mixture was poured into water (125 mL), and the resultant solution was extracted with ether (7 × 100 mL). The ether extracts were washed with saturated NaCl solution (50 mL), dried (Na_2SO_4), and concentrated to afford 11.01 g of a mixture of enol ether **4**, triphenyl phosphine oxide, and unreacted (methoxymethyl)triphenylphosphonium chloride. Without further purification the crude product was dissolved in THF (125 mL) and concentrated HCl (2.3 mL) was added. This was stirred at 25 °C until TLC (benzene/hexane, 7:3) showed no enol ether remaining (ca. 2 h). Water (125 mL) was added, and the resultant solution was extracted with $CHCl_3$ (7 × 100 mL). The $CHCl_3$ layers were washed with saturated NaCl solution (50 mL) and saturated $NaHCO_3$ solution (50 mL), dried (Na_2SO_4), and concentrated. Silica gel (250 g) column chromatography of the residue (10.7 g) with benzene/hexane (1:1) as the eluent afforded pure **3** (2.08 g, 73% from ketone **5**) as a clear oil: IR (film) 2970, 2850, 1740, 760, 670 cm^{-1}; ^1H NMR δ 9.5 (d, J = 4 Hz, 1 H, CHO), 7.3–7.0 (m, 4 H, aromatic), 3.1–1.3 (m, 12 H), 1.13 (s, 3 H, C-4a-CH_3); ^{13}C NMR, δ 204.46 (d, CHO), 147.1 (s, aromatic), 134.9 (s, aromatic), 129.4 (d, aromatic), 125.9 (2C, d, aromatic), 124.4 (d, aromatic), 51.3 (d, C-1), 41.7 (d, C-10a), 37.3 (t), 36.4 (s, C-4a), 28.9 (t), 26.5 (t), 22.9 (t), 22.6 (t), 20.7 (q, CH_3); MS, m/z 228 (M^+), 143, 117 (base).

1,4aβ-Dimethyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene-1β-carboxaldehyde (2). The method of Ziegler and Kloek[1f] was used. A solution of aldehyde **3** (0.205 g, 0.9 mM) in dry benzene (3 mL) was added to *tert*-butyl alcohol (4.1 mL) in a three-necked, round-bottomed flask (25 mL) under argon. Methyl iodide (0.34 g, 2.4 mM) was added, followed by dropwise addition of 0.5 N potassium *tert*-butoxide in *tert*-butyl alcohol (3.2 mL, 2.4 mM). When addition was complete, the reaction mixture stirred at 25 °C under argon for 2 h. Water (5 mL) was added to the reaction mixture, and it was extracted with $CHCl_3$ (7 × 7 mL). The $CHCl_3$ phases were washed with saturated NaCl solution (2 × 7 mL), dried, and concentrated to give yellow solid (0.192 g). Recrystallization (methanol) of the solid and chromatography of the mother liquors afforded **2** as a white crystalline solid, mp 93–95 °C: IR ($CHCl_3$) 2930, 2850, 1715, 755, 725 cm^{-1}; ^1H NMR δ 9.8 (br s, 1 H, CHO), 7.3–7.0 (m, 4 H, aromatic), 3.01–1.3 (m, 11 H), 1.11 (s, 3 H, C-1-CH_3), 1.07 (s, 3 H, C-4a-CH_3); MS, m/z 242 (M^+), 199, 143, 117 (base).

1,4aβ-Dimethyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene-1β-carboxylic Acid (1b) and Methyl Ester (15). The method of Ziegler and Kloek[1f] was used. Aldehyde **2** (0.192 g, 0.79 mM) was dissolved in acetone (15 mL) and cooled to 0 °C. Jones reagent (1.5 mL) was added in a dropwise manner with vigorous mechanical stirring. The reaction mixture gradually warmed to 25 °C and was stirred until TLC (ethyl acetate/hexane, 1:9) showed that no aldehyde remained (ca. 8$^1/_2$ h). Isopropyl alcohol (2 mL) was added to consume excess oxidant, and the acetone solution was decanted from the green Cr(III) salts. These salts were then extracted with ether (2 × 15 mL). The organic phases were combined, dried (Na_2SO_4), and concentrated in vacuo to a dark green solid (0.186 g). The solid was dissolved in ether (25 mL) and washed with an aqueous solution of 10% K_2CO_3 (4 × 5 mL). The basic aqueous phase was cooled to 0 °C, acidified to ca. pH 1 with 0.1 N HCl, and extracted with ether (10 × 5 mL). The ether extracts were dried (Na_2SO_4) and concentrated to afford **1b** as a white solid (0.116 g, 56%). Recrystallization from ether gave colorless plates, mp 230–232 °C (lit.[1i] mp 232–234 °C). Treatment of acid **1b** with etheral CH_2N_2 afforded methyl ester **15** as a white solid. Recrystallization from methanol afforded white crystals, mp 126–127 °C (lit.[1i] mp 126–127 °C, mp 127.5–128.5 °C, mp 130–131 °C): IR ($CHCl_3$) 2950, 1740 cm^{-1}; ^1H NMR δ 7.5–7.0 (m, 4 H, aromatic), 3.75 (s, 3 H, OCH_3), 3.0–1.5 (m, 11 H), 1.30 (s, 3 H, C-1-CH_3), 1.05 (s, 3 H, C-4a-CH_3); MS, m/z 272 (M^+), 257 (M − 15), 141, 117 (base).

1-Ethylidene-4aβ-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (13). The method of Ziegler and Kloek[1f] was used. Sodium dimsyl was generated in situ from sodium hydride (1.79 g, 39.7 mM) and dry dimethyl sulfoxide (50 mL) as described. A solution of ethyltriphenylphosphonium bromide (14.85 g, 40.0 mM) in dry dimethyl sulfoxide (35 mL) was added, the mixture was stirred for 10 min, followed by addition of ketone **5** (2.65 g, 12.4 mM) in dry dimethyl sulfoxide (20 mL). The reaction mixture then stirred at ambient temperature (ca. 23 °C) for 21 h, at 60 °C for 1 h, and at ambient temperature for 2 h. For workup, the reaction mixture was poured into water (200 mL), and the resultant mixture was extracted with ether (8 × 100 mL). The extracts were dried (Na_2SO_4) and concentrated to afford a solid (11.39 g). Chromatography of the solid on silica gel (241 g) with benzene/hexane (1:1) as the eluent afforded pure **13** as an oil (1.94 g, 69%): IR (film) 2940, 1490, 1440, 760, 725 cm^{-1}; ^1H NMR δ 7.5–7.0 (m, 4 H, aromatic), 5.4–5.0 (br q, J = 7 Hz, 1 H, vinyl H), 3.1–1.1 (m, 11 H), 1.73 (d, J = 7 Hz, 3 H, vinyl CH_3), 1.00 (s, 3 H, C-4a-CH_3); MS, m/z 226 (M^+), 211 (M − 15), 129 (base).

Anal. Calcd for $C_{17}H_{22}$: C, 90.20; H, 9.80. Found: C, 90.28; H, 9.80.

1β-(1-Hydroxyethyl)-4aβ-methyl-1,2,3,4,4a,9,10,10aα-octahydro-1α-phenanthrol (12). The method of Fetizon et al.[5] was used. Olefin **13** (0.486 g, 2.15 mM) was dissolved in dry pyridine (30 mL), and a solution of osmium tetraoxide (0.60 g, 2.36 mM)

(7) McNair, H. M.; Bonelli, E. J. In "Basic Gas Chromatography", 5th ed.; Varian: Palo Alto, 1965, Chapter 7.

in dry pyridine (6 mL) was added. The reaction mixture was placed in the dark at ambient temperature (ca. 25 °C) for 24 h. A solution of sodium bisulfite (1.2 g) in water (20 mL) and pyridine (15 mL) was added, and the resultant mixture was stirred vigorously at ambient temperature for 2 h and then extracted with $CHCl_3$ (8 × 20 mL). The $CHCl_3$ extracts were washed with 0.5 N HCl (3 × 33 mL), saturated sodium bicarbonate solution (25 mL) and brine (2 × 25 mL), dried (Na_2SO_4), and concentrated to give an oil (0.571 g). Chromatography of the crude product on silica gel (50 g) with ethyl acetate/hexane (1:4) as the eluent afforded diol **12** (0.401 g, 71%) as a white solid. Recrystallization of the solid from hexane/ether afforded white needles, mp 122–123 °C: IR (KBr) 3340, 2940, 980, 760, 740 cm^{-1}; ^1H NMR δ 7.4–7.0 (m, 4 H, aromatic), 4.6–4.1 (q, J = 6 Hz, 1 H, CH_3CHOH–), 3.1–1.1 (m, 14 H), 2.37 (br s, D_2O exchangeable, 2 H, glycol H), 1.32 (s, 3 H, C-4a-CH_3); MS, m/z 242 (M − 18), 131 (base).

Anal. Calcd. for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.09; H, 9.50.

1β-Acetyl-4aβ-methyl-1,2,3,4,4a,9,10,10aα-octahydro-1α-phenanthrol (11). Diol **12** (0.244 g, 0.94 mM) was dissolved in acetone (30 mL) and cooled to 0 °C. Jones reagent (0.23 mL, 0.61 mequiv) was slowly added in a dropwise manner until TLC (ethyl acetate/hexane, 2:3) indicated that little diol remained (ca. 1 h). Isopropyl alcohol (1 mL) was added, and the organic phase was decanted from the chromium salts. The salts were extracted with ether (3 × 10 mL), and the organic phases were combined, dried (Na_2SO_4), and concentrated to afford an oil (0.203 g). Chromatography on silica gel with ethyl acetate/hexane (3:7) as the eluent afforded hydroxy ketone **11** (0.056 g, 23%) as a white solid, mp 130–132 °C: IR (KBr) 3420, 2940, 1695, 760, 740 cm^{-1}; ^1H NMR δ 7.6–6.8 (m, 4 H, aromatic H), 3.09–1.1 (m, 12 H), 2.23 (s, 3 H, CH_3CO–), 1.00 (s, 3 H, C-4a-CH_3).

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.81; H, 8.31.

The method of Omura and Swern was used.[6] A stock solution of 1.4 g (0.011 mol) of oxalyl chloride and 1.9 g (0.024 mol) of dimethyl sulfoxide in 30 mL of methylene chloride was prepared and maintained at −60 °C in a dry ice–chloroform bath. To 1.63 mL of that solution maintained at −60 °C was added slowly 0.130 g (0.5 mmol) of diol **12** in 1.0 mL of methylene chloride. After the addition was complete, the reaction mixture was stirred for 25 min and 0.24 mL (2.4 m mol) of triethylamine was added dropwise. After addition was complete, the cooling bath was removed, and water (3.0 mL) was added. Stirring was continued for 30 min, the organic layer was separated, the water layer was re-extracted with methylene chloride (2 × 3 mL), and the organic extracts were combined, dried (Na_2SO_4), and evaporated. Chromatography of the residue on 30 g of silica gel 60 with hexane–ethylacetate mixtures as eluent provided 0.050 g of hydroxy ketone **11** and 0.070 g of recovered diol **12**; yield, 84% based on recovered diol **12**.

1β-Acetyl-4aβ-methyl-1,2,3,4,4a,9,10,10aα-octahydro-1α-phenanthrol, Methanesulfonate Ester (9). Hydroxy ketone **11** (0.060 g, 0.23 mM) was dissolved in dry pyridine (4 mL), and methanesulfonyl chloride (0.0798 g, 0.7 mM) was added in a dropwise manner. This sat in the dark at 5 °C for 42 h before addition of ice-cold water (4 mL). The aqueous phase was extracted with $CHCl_3$ (5 × 5 mL). The organic phase was washed with brine (5 mL), ice-cold 1 N H_2SO_4 (10 mL), and brine (5 mL), dried (Na_2SO_4), and concentrated to give an oil (0.59 g). ^1H NMR indicated an incomplete reaction, so this material was redissolved in pyridine (4 mL), and methanesulfonyl chloride (0.0798 g, 0.7 mM) was again added. The reaction mixture sat at 5 °C for 12 h and then at ambient temperature for 26 h. An identical workup as before afforded **9** as a brown oil. The reaction mixture was used in the subsequent Favorskii reaction without any further purification: ^1H NMR δ 7.4–7.0 (m, 4 H), 3.1 (s, 3 H, $-SO_2CH_3$), 3.0–1.2 (m, 11 H), 2.23 (s, 3 H, $-COCH_3$), 1.0 (s, 3 H, C-4a-CH_3).

Methyl 1β,4aβ-Dimethyl-1,2,3,4,4a,9,10,10aα-octahydrophenanthrene-1α-carboxylate (10). The method of House and Gilmore was used.[3] A 0.0012 mol/mL solution of sodium methoxide in dimethoxyethane (DME) was prepared by dissolving sodium (0.132 g, 0.0057 g-atom) in methanol (2 mL) and adding dry DME (46 mL). To this NaOMe solution (7 mL, 0.84 mM) was added a solution of mesylate **9** (0.0693 g, 0.21 mM) in dry DME (2 mL). The reaction mixture was then stirred at ambient temperature under argon for 3 h while it was monitored by TLC. After an additional 8 h, TLC showed no further change, so the reaction was worked up by addition of H_2O (7 mL) and extraction with ether (7 × 5 mL). The ether layers were dried (Na_2SO_4) and concentrated to afford a brown oil (0.0219 g). The aqueous phase was acidified to ca. pH 2 with cold 6 N H_2SO_4 and extracted with ether (5 × 5 mL). The ether layers were dried (Na_2SO_4) and concentrated to afford an oil (0.0074 g) whose TLC (ethyl acetate/hexane, 1:4) was the same as above. The oils were combined and preparative TLC afforded **10** as a solid, mp 111–112 °C (lit.[11] mp 114–115 °C): IR ($CHCl_3$) 2950, 1740, 760, 740 cm^{-1}; ^1H NMR δ 7.26–7.04 (m, 4 H), 3.67 (s, 3 H, OCH_3), 3.0–1.3 (m, 11 H), 1.28 (s, 3 H, C-1-CH_3), 1.22 (s, 3 H, C-4a-CH_3); MS, m/z 272 (M^+), 257 (M − 15), 197 (base).

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Stereoselective Synthesis of 4a-Methyloctahydrophenanthrenes: A Novel Approach. 2. C-1 Substituted Series

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We report the stereoselective conversion of 4a-methyl-2,4a,9,10-tetrahydrophenanthrene (**1**), readily available from phenanthrene by reductive alkylation, via 4a-methyl-2,3,4,4a,9,10-hexahydrophenanthrene (**2**), into several C-1 substituted compounds. Chemical verification of stereochemistry is accomplished and the proton magnetic resonance characteristics of the substance are presented and discussed.

Continuing our studies of the preferred conformations of monosubstituted 4a-methyloctahydrophenanthrenes in solution,[1] we have now completed the stereospecific syntheses of all the possible C-1 4a-methyloctahydrophenanthrene isomeric amines and alcohols. In the present discussion the terms *cis* and *trans* will refer only to the A/B juncture; cis, 10aβ-H; trans, 10aα-H. The strategy for the proposed synthesis is shown in Scheme I and implies the preparation of the monoolefin, 4a-methyl-

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