tallization from absolute ethanol. Pure **14** (466 mg, 63%) was thereby obtained as colorless platelets: mp 120.0–120.5 °C; IR (KBr) 1549 (vs), 1382 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.64 (*AB*, J_{AB} = 10.8 Hz, 1 H), 2.01 (*AB*, J_{AB} = 10.8 Hz, 1 H), 2.8–3.3 (m, 8 H), 4.97 (t, *J* = 3.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 41.3 (d), 42.8 (d), 43.3 (t), 44.6 (d), 44.9 (2 C, d), 49.6 (d), 54.7 (d), 59.1 (d), 84.7 (d), 121.2 (s); mass spectrum, *m/e* (relative intensity) (no molecular ion), 159 (100).

Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40. Found: C, 64.30; H, 5.47.

Sodium Borohydride Reduction of 13. A suspension of **13** (3.00 g, 10.6 mmol) in 95% aqueous ethanol (300 mL) was cooled to 0 °C via application of an external ice–salt bath. To the vigorously stirred suspension was added a solution of sodium borohydride (2.0 g, 52 mmol) in 60% aqueous ethanol (50 mL). The resulting mixture was stirred for 5 min, at which time the external cold bath was removed. The reaction mixture was then stirred at room temperature for 2 h. The reaction was quenched via gradual addition of glacial acetic acid (15 mL), which resulted in the production of an intense blue color. Workup of the reaction mixture followed by ozonolysis as described above for the corresponding reaction of **8b** afforded pure **14** (1.55 g, 73%). The material thereby obtained was identical in all respects with that obtained previously via sodium borohydride reduction of **8b** followed by ozonolysis (vide supra).

Acknowledgment. We gratefully acknowledge the assistance of Dr. Sanjay Basak with the characterization of **14**. We thank the U.S. Army Armament Research and Development Center, Picatinny Arsenal, NJ (Contract DAAA21-86-C-0091), the Air Force Office of Scientific Research (Grant AFOSR-84-0085), the Robert A. Welch Foundation (Grant B-963), and the North Texas State University Faculty Research Committee for financial support of this study.

Registry No. **1**, 2958-72-7; **2**, 34052-35-2; **3**, 112482-28-7; **4**, 56143-85-2; **5**, 112482-29-8; **6**, 112482-30-1; **7**, 112571-23-0; **8a**, 112482-31-2; **8b**, 112571-24-1; **10**, 111933-65-4; **11**, 80707-70-6; **12**, 111933-64-3; **13**, 112482-32-3; **14**, 112482-33-4.

Preparation of the Chiral Hydronaphthalene Fragment of Kijanolide and Tetronolide

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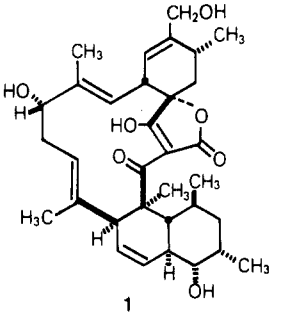
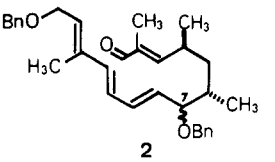
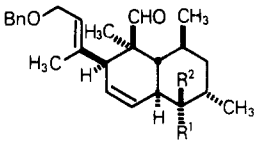
In the course of their synthetic study on kijanolide (**1**)[1] and the related natural products tetronolide[2] and chlorothricolide,[3] Marshall and his co-workers have introduced an efficient method for the construction of the *trans*-octalin fragments that utilizes intramolecular Diels–Alder cyclization of conjugated aldehydes which proceeds in a highly endo-selective manner.[4] Of particular interest is the result obtained with a C(7) epimeric mixture of racemic tetraenal **2**.[5] Treatment of **2** with Me_2AlCl at low temperature afforded a 1:1 mixture of the carbinyl epimers **3a,b** in high yield, and it was suggested that a diastereomerically homogeneous sample of **2** with the correct configuration (7*S*) would produce compound **3b** exclusively. This paper records an asymmetric synthesis of **13** and **15**, optically active analogous of **3b** which have two different O-protecting groups, according to the method of Marshall. This result, together with our previous achievements in the syntheses of the spirotetronic acid fragments[6] and a macrocyclic model,[7] would make a great advance in the total synthesis of **1** and tetronolide.



1



2



3a R^1 = H, R^2 = OBn
3b R^1 = OBn, R^2 = H

To establish the three chiral centers in the Diels–Alder precursors **11** and **12**, we employed the trideoxy sugar **4**[8] as the starting material. Desilylation of compound **4** followed by Swern oxidation of the resulting alcohol **5** gave aldehyde **6**. Horner–Emmons reaction of **6** with the phosphonate **8**, which was prepared from 4-(benzyloxy)-2-methyl-2(*E*)-butenal (**7**)[5] as outlined in Scheme I, afforded the *E,E,E* triene **9** as the only isolable diastereomer in 55% overall yield from **4**. Use of more readily available methyl 6-(diethylphosphono)-3-methyl-2(*E*),4(*E*)-hexadienoate[9] in the condensation with **6** resulted in formation of an inseparable mixture of the terminal double bond isomers. The functionalized pyranoside **9** was then treated with aqueous acetic acid in THF to give a sensitive lactol, which was immediately allowed to react with $Ph_3P{=}C(Me)COOEt$ in refluxing acetonitrile to give tetraenoate **10** (46% for the two steps). This compound was transformed into MOM- and TBS-protected tetraenals (**11** and **12**), respectively, by conventional three-step procedures, O protection followed by reduction (i-Bu_2AlH)/oxidation (pyridinium chlorochromate (PCC)).

Treatment of **11** with 1.0 equiv of Me_2AlCl in CH_2Cl_2 at −80 to −40 °C produced a mixture of cycloadducts, from which the desired octalin (−)-**13** and its diastereomer **14** were isolated by silica gel MPLC in 65% and 22% yields, respectively. The structures of these endo-mode adducts (trans ring juncture) were assigned by high-field ^1H NMR

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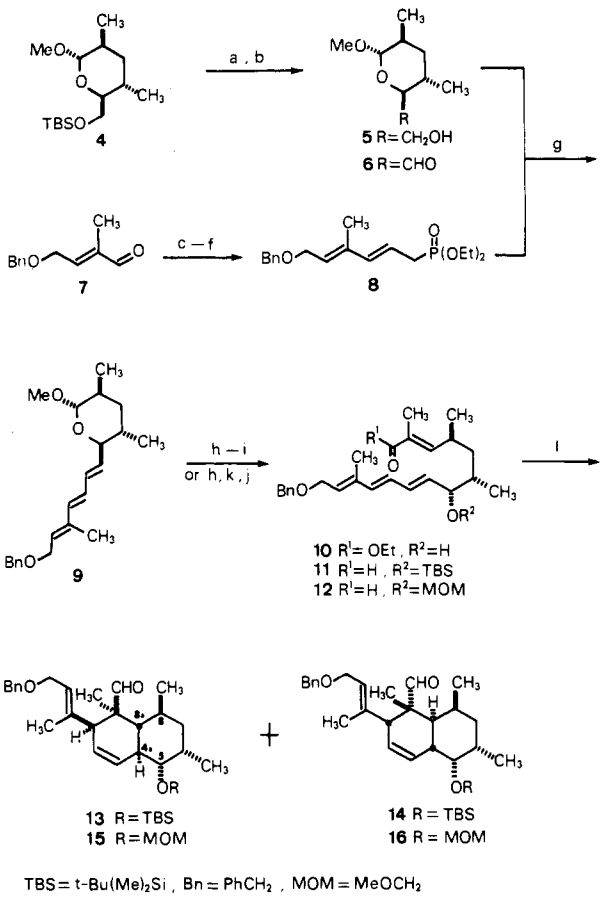
Scheme I[a]



[a] (a) n-Bu_4NF, THF; (b) Me_2SO, $(COCl)_2$, CH_2Cl_2, then NEt_3; (c) $(EtO)_2P(O)CH_2COOMe$, NaH, THF; (d) i-Bu_2AlH, Et_2O; (e) NBS, Me_2S, CH_2Cl_2;[10] (f) $(EtO)_3P$; (g) KO-t-Bu, THF; (h) AcOH, H_2O, THF, then $Ph_3P{=}C(Me)COOEt$, PhH; (i) t-$BuMe_2SiCl$, imidazole, DMF; (j) i-Bu_2AlH, Et_2O, then PCC, AcONa, CH_2Cl_2; (k) $MeOCH_2Cl$, i-Pr_2NEt, CH_2Cl_2; (l) Me_2AlCl, CH_2Cl_2.

spectral analysis; $J_{4a,8a} = J_{4a,5} = J_{8,8a} = 10.4$ Hz for **13**, $J_{4a,8a} = 10.5$ Hz for **14**. Formation of an appreciable amount of unwanted isomer **14** is not unexpected. It has been reported that, in the intramolecular cycloaddition of 7-alkoxy-2-methyl-2,8,10-undecatrienals, the 7-OTBS group exhibits a marked preference for an axial orientation in contrast to benzyl and methoxymethyl (MOM) derivatives.[4] Use of the MOM ether **12** did improve the isomer ratio to give a 97:3 mixture of **15** and **16**, but the product yield (ca. 40% for **15**) was unacceptable. The low yield of this cycloaddition may be attributed to the sensitivity of the MOM ether under the Lewis acid conditions.

Experimental Section

IR spectra were recorded on a JASCO IRA-1 grating spectrometer and were calibrated with 1601-cm^{-1} absorption of polystyrene. ^1H NMR spectra were taken on a JEOL PMX-60SI (60 MHz), GX-270 (270 MHz), or GX-400 (400 MHz) spectrometer in $CDCl_3$ unless otherwise noted. Chemical shifts are expressed in δ_{ppm} downfield from internal Me_4Si. Resonance patterns are described as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. Low- and high-resolution mass spectra (EI-MS) were obtained with a JEOL JMS-D-300 spectrometer combined with a JEOL JMA-2000 data processing system. Optical rotations were measured on a JASCO DIP-140 polarimeter. Liquid chromatography under medium pressures (MPLC) was carried out with a Waters Model 6000A chromatograph by using a prepacked column (22 mm × 300 mm, 10-μm silica gel) (Kusano Kagakukikai Co.). For routine chromatography, the following adsorbents were used: Fuji-Davison silica gel BW-200 (150-325 mesh) for column chromatography; Wako precoated silica gel 70 F-254 plates for analytical thin-layer chromatography. Preparative-scale GLC was performed with a Shimadzu GC-6A apparatus by TCD mode using a stainless steel column of 5 mm × 1 m packed with 10% OV-17 on Shimalite (60–80 mesh). Dry solvents and reagents were obtained by using standard procedures. Anhydrous $MgSO_4$ was used for drying all organic solvent extracts in workup, and removal of the solvents was performed with a rotary evaporator.

(2*S*,3*S*,5*S*,6*S*)-6-[[(*tert*-Butyldimethylsilyl)oxy]methyl]-2-methoxy-3,5-dimethyltetrahydropyran (4). This compound was prepared from methyl 6-*O*-(*tert*-butyldimethylsilyl)-2,3-dideoxy-α-D-*glycero*-hex-2-enopyranosid-4-ulose[8c] according to the procedure of Fraser-Reid[8b] (22% yield for five steps).

(2*S*,3*S*,5*S*,6*R*)-2-Methoxy-3,5-dimethyltetrahydropyran-6-methanol (5). A 1.0 M THF solution of n-Bu_4NF (3.82 mL) was added to **4** (1.00 g, 3.47 mmol), and the solution was stirred at room temperature for 20 min. It was diluted with CH_2Cl_2 (30 mL), and then water (10 mL) was added. Phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (5 mL × 3). The combined organic phases were washed with brine (5 mL) and concentrated to ca. 5 mL with the temperature kept below 30 °C. Further concentration results in considerable loss of the product **5** by codistillation with the solvent, and therefore the CH_2Cl_2 solution was used for the next step. An analytical sample of **5** was obtained by preparative GLC (t_R 5.0 min, 70 °C): R_f 0.37 (1:1 hexane–AcOEt); $[\alpha]^{23}_D$ +109.31° (*c* 1.139, $CHCl_3$); IR (neat) 3460 cm^{-1}; ^1H NMR (270 MHz) δ 0.82 (3 H, d, J = 6.3 Hz, Me-5), 1.06 (3 H, d, J = 7.3 Hz, Me-3), 1.37 (1 H, ddd, J = 9.8, 2.7, 2.7 Hz, H-4eq), 1.67 (1 H, ddd, J = 9.8, 9.8, 4.6 Hz, H-4ax), 1.81 (1 H, m, H-5), 1.87 (1 H, m, H-3), 2.42 (1 H, dd, J = 7.3, 5.3 Hz, OH), 3.36 (3 H, s, OMe), 3.41 (1 H, ddd, J = 10.4, 6.4, 2.7 Hz, H-6), 3.58 (1 H, ddd, J = 11.4, 6.4, 5.3 Hz, CH*H*-6), 3.74 (1 H, ddd, J = 11.4, 7.3, 2.7 Hz, CH*H*-6), 4.41 (1 H, br s, H-2); MS, *m/e* 143.1071 (M^+ − 31, calcd 143.1071), 121, 105, 86, 18 (base peak).

(2*S*,3*S*,5*S*,6*R*)-2-Methoxy-3,5-dimethyltetrahydropyran-6-carboxaldehyde (6). Me_2SO (1.08 g, 13.88 mmol) was added dropwise to a stirred solution of oxalyl chloride (890 mg, 6.94 mmol) in CH_2Cl_2 (25 mL) at −60 to −50 °C. After 15 min, the CH_2Cl_2 solution of crude **5** obtained above was added at −60 °C, and the mixture was allowed to warm to −30 °C over 28 min before addition of triethylamine (3.14 g, 31.1 mmol). The reaction mixture was allowed to warm to room temperature over 10 min and then stirred for 30 min. The mixture was treated with ether (20 mL) and water (10 mL), and phases were separated. The aqueous phase was extracted with ether (10 mL × 3). The combined organic phases were washed with brine (5 mL × 3), dried, and concentrated. The residue was distilled with a Kugelrohr apparatus to give crude **6** (690 mg) as a colorless oil, bp 60–80 °C (4 Torr) contaminated with ca. 20% disiloxane. An analytical sample was obtained by preparative GLC (t_R 4.5 min, 65 °C): $[\alpha]^{23}_D$ +43.65° (*c* 0.944, $CHCl_3$); R_f 0.67 (1:1 hexane–AcOEt); IR (neat) 1735 cm^{-1}; ^1H NMR (270 MHz) δ 0.96 (3 H, d, J = 6.6 Hz, Me-5), 1.08 (3 H, d, J = 7.1 Hz, Me-3), 1.44 (1 H, ddd, J = 13.2, 3.7, 3.7 Hz, H-4eq), 1.72 (1 H, ddd, J = 13.2, 11.5, 4.6 Hz, H-4ax), 1.80–2.02 (2 H, m, H-3 and H-5), 3.38 (3 H, s, OMe), 3.75 (1 H, dd, J = 10.3, 2.0 Hz, H-6), 4.47 (1 H, br s, H-2), 9.65 (1 H, d, J = 2.0 Hz, CHO); MS, *m/e* 172.1107 (M^+, calcd 172.1099), 157, 143, 141, 111, 18 (base peak).

Diethyl (2*E*,4*E*)-[6-(Benzyloxy)-4-methyl-2,4-hexadienyl]phosphonate (8). A stirred suspension of NaH (60% in mineral oil, 2.57 g, 64.5 mmol, washed with dry THF) in dry THF (7 mL) was cooled with ice–water, and methyl (diethylphosphono)acetate (13.5 g, 64.5 mmol) was added over 5 min. After being stirred at room temperature for 10 min, the mixture was cooled again with ice–water, and a solution of **7** (10.19 g, 53.6

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mmol) in dry THF (35 mL) was introduced over 8 min. The reaction mixture was then stirred at room temperature for 30 min before being poured into ice–water (20 mL) and ether (40 mL). Phases were separated, and the aqueous phase was extracted with ether (20 mL × 2). The combined organic phases were washed with brine (5 mL × 3), dried, and concentrated to give methyl 6-(benzyloxy)-4-methyl-2(*E*),4(*E*)-hexadienoate (15.66 g) as an essentially homogeneous oil: R_f 0.44 (4:1 hexane–AcOEt); ^{1}H NMR (60 MHz) δ 1.80 (3 H, s, Me-4), 3.50 (3 H, s, OMe), 4.20 (2 H, d, J = 6 Hz, H-6), 4.60 (2 H, s, OCH_2Ph), 5.90 (1 H, d, J = 16 Hz, H-1), 6.10 (1 H, t, J = 6 Hz, H-5), 7.30 (1 H, d, J = 16 Hz, H-3), 7.40 (5 H, s, Ar H).

A stirred solution of the above hexadienoate (15.66 g) in dry ether (50 mL) under nitrogen was cooled to −70 °C, and a 1.0 M hexane solution of *i*-Bu_2AlH (118 mL) was added over 7 min. After continued stirring at the same temperature for 20 min, the reaction mixture was quenched with MeOH (100 mL). The mixture was filtered through a layer of Celite, and then the remaining solid was washed with AcOEt (150 mL). The combined filtrates were concentrated, and the residual oil was subjected to chromatography (silica gel, 230 g; elution with 1:1 hexane–AcOEt) to afford 6-(benzyloxy)-4-methyl-2,4-hexadienol (10.32 g, 88%) as a colorless oil: R_f 0.40 (1:1 hexane–AcOEt); ^{1}H NMR (60 MHz) δ 1.60 (1 H, s, OH), 1.80 (3 H, s, Me-3), 4.20 (4 H, d, J = 6 Hz, H-1 and H-6), 4.55 (2 H, s, OCH_2Ph), 5.60–6.60 (3 H, m, H-2, H-3, and H-5), 7.40 (5 H, s, Ar H).

Dimethyl sulfide (4.91 g, 79.0 mmol) was added over 5 min to a stirred suspension of *N*-bromosuccinimide (11.8 g, 66.3 mmol) in CH_2Cl_2 (200 mL) cooled with ice–water. The mixture was cooled to −30 °C, a solution of the above hexadienol (9.61 g, 44.1 mmol) in CH_2Cl_2 (40 mL) was added dropwise over 10 min, and then the mixture was stirred at the ice–water temperature for 60 min. The reaction mixture was diluted with CH_2Cl_2 (200 mL), washed with cold brine, dried, and concentrated to give the corresponding bromide (14.58 g).

This material was dissolved in $(EtO)_3P$ (12.89 g, 77.7 mmol), and the solution was heated at 100 °C for 35 min. Low-boiling substances were removed at ~135 °C (~0.2 Torr), and the residue was subjected to chromatography (silica gel, 180 g, elution with 1:4 hexane–AcOEt) to give **8** (12.54 g, 84%) as a colorless oil: R_f 0.31 (AcOEt); IR (neat) 1250 cm^{-1}; ^{1}H NMR (270 MHz) δ 1.34 (6 H, t, J = 7.1 Hz, OCH_2CH_3), 1.76 (3 H, s, Me-4), 2.66 (2 H, dd, J = 22.3, 7.3 Hz, H-1), 4.10 (4 H, dq, J = 7.1, 7.1 Hz, OCH_2CH_3), 4.14 (2 H, d, J = 8.1 Hz, H-6), 4.51 (2 H, s, OCH_2Ph), 5.52–5.70 (2 H, m, H-2, H-5), 6.22 (1 H, dd, J = 15.9, 4.5 Hz, H-3), 7.35 (5 H, m, Ar H); MS, m/e 338.1642 (M$^+$, calcd 338.1645), 247, 231, 219, 191 (base peak).

(2*S*,3*S*,5*S*)-6-[(1*E*,3*E*,5*E*)-7-(Benzyloxy)-5-methyl-1,3,5-heptatrienyl]-2-methoxy-3,5-dimethyltetrahydropyran (9). To a stirred solution of the crude sample of **6** (690 mg) obtained above and **8** (1.41 g, 4.16 mmol) in dry THF (6 mL) at −78 °C under nitrogen was added a cooled solution (−78 °C) of *t*-BuOK (470 mg, 4.16 mmol) in dry THF (12 mL) over 3 min. The mixture was allowed to warm to −45 °C over 45 min and then diluted with ether (10 mL) before addition of water (10 mL). Phases were separated, and the aqueous phase was extracted with ether (10 mL × 3). The combined organic phases were washed with brine (5 mL × 4), dried, and concentrated. The residue was subjected to chromatography (silica gel, 40 g; elution with 7:1 hexane–AcOEt) to give **9** (680 mg, 55%) as a colorless oil: $[\alpha]^{23}_D$ +57.61° (*c* 2.804, $CHCl_3$); R_f 0.56 (4:1 hexane–AcOEt); IR (neat) 1455, 755 cm^{-1}; ^{1}H NMR (270 MHz) δ 0.78 (3 H, d, J = 6.1 Hz, Me-5), 1.08 (3 H, d, J = 7.1 Hz, Me-3), 1.39 (1 H, dd, J = 8.5, 2.0 Hz, H-4eq), 1.77 (3 H, s, Me-5′), 1.60–1.92 (3 H, m, H-3, H-4ax, and H-5), 3.36 (3 H, s, OMe), 3.77 (dd, J = 9.3, 8.1 Hz, H-6), 4.17 (2 H, d, J = 6.6 Hz, H-7′), 4.41 (1 H, s, H-2), 4.51 (2 H, s, OCH_2Ph), 5.68 (1 H, t, J = 6.6 Hz, H-6′), 5.70 (1 H, dd, J = 15.4, 8.1 Hz, H-1′), 6.18–6.37 (3 H, m, H-2′, H-3′, and H-4′), 7.33 (5 H, m, Ar H); MS, m/e 356.2361 (M$^+$, calcd 356.2350), 267, 248, 143, 91 (base peak).

Ethyl (4*S*,6*S*,7*S*)-(2*E*,8*E*,10*E*,12*E*)-14-(Benzyloxy)-7-hydroxy-2,4,6,12-tetramethyltetradeca-2,8,10,12-tetraenoate (10). A solution of **9** (1.00 g, 2.81 mmol) in THF (8 mL) and water (8 mL) was heated at 60–65 °C for 70 min after addition of acetic acid (12 mL). The mixture was cooled to room temperature, and AcOEt (20 mL) and a cold aqueous solution (40 mL) of NaOH (8.4 g) were added. Phases were separated, and the aqueous phase was extracted with AcOEt (10 mL × 3). The combined organic phases were washed with brine (5 mL × 2), dried, and concentrated. The residual oil was dissolved in dry acetonitrile (9 mL), and the solution was heated at 80–85 °C for 16 h after addition of Ph_3P=C(Me)COOEt (5.41 g, 14.9 mmol). The mixture was concentrated, and the residue was extracted with ether. Removal of the solvent followed by chromatography (silica gel, 50 g; elution with 5:3:2 hexane–CH_2Cl_2–ether) of the residue afforded **10** (490 mg, 46%) as a pale yellow oil, R_f 0.24 (4:1 hexane–AcOEt).

(4*S*,6*S*,7*S*)-(2*E*,8*E*,10*E*,12*E*)-14-(Benzyloxy)-7-[(*tert*-butyldimethylsilyl)oxy]-2,4,6,12-tetramethyltetradeca-2,8,10,12-tetraenal (11). Compound **10** (530 mg, 1.24 mmol) was treated with *t*-$BuMe_2SiCl$ (281 mg, 1.87 mmol) and imidazole (254 mg, 3.73 mmol) in dry DMF (2 mL) for 3.5 h at room temperature. The crude product obtained by extractive workup with ether was purified by chromatography (silica gel, 45 g; elution with 6:1 hexane–AcOEt) to give the TBS ether of **10** (470 mg, 70%) as a colorless oil: $[\alpha]^{23}_D$ +39.37° (*c* 0.666, $CHCl_3$); R_f 0.65 (3:1 hexane–AcOEt); IR (neat) 1710 cm^{-1}; ^{1}H NMR (270 MHz) δ −0.01, 0.01 (each 3 H, s, $SiMe_2$), 0.84 (3 H, d, J = 7.0 Hz, Me-4), 0.89 (9 H, s, *t*-Bu), 0.95 (3 H, d, J = 6.4 Hz, Me-6), 1.18 (1 H, ddd, J = 12.2, 7.2, 5.6 Hz, H-5), 1.30 (3 H, t, J = 7.1 Hz, OCH_2CH_3), 1.44 (1 H, ddd, J = 12.2, 6.6, 4.7 Hz, H-5), 1.55-1.70 (1 H, m, H-6), 1.79 (3 H, s, Me-12), 1.84 (3 H, d, J = 1.2 Hz, Me-2), 2.55 (1 H, m, H-4), 3.97 (1 H, dd, J = 6.4, 6.1 Hz, H-7), 4.17 (2 H, d, J = 6.8 Hz, H-14), 4.18 (2 H, q, J = 7.1 Hz, OCH_2CH_3), 4.52 (2 H, s, OCH_2Ph), 5.62 (1 H, dd, J = 14.3, 6.4 Hz, H-8), 5.66 (1 H, t, J = 6.8 Hz, H-13), 6.10–6.30 (3 H, m, H-9, H-10, and H-11), 6.57 (1 H, dd, J = 8.5, 1.2 Hz, H-3), 7.34 (5 H, m, Ar H); MS, m/e 540.3654 (M$^+$, calcd 540.3632), 432, 357, 149, 91 (base peak).

To a stirred solution of the above TBS ether (425 mg, 0.787 mmol) in dry ether (2.5 mL) at −70 °C was added dropwise a 1.0 M hexane solution of *i*-Bu_2AlH (1.73 mL) over 2 min. After 9 min, the reaction mixture was diluted with ether (5 mL) and quenched with MeOH (3 mL). The mixture was filtered through a layer of Celite, and the filtrate and ether washings were combined and concentrated. The residue was dissolved in dry CH_2Cl_2 (3 mL), and the solution was stirred at room temperature and treated with PCC (254 mg, 1.18 mmol) and NaOAc (97 mg, 1.18 mmol) in the presence of Celite (260 mg). After 70 min, the reaction mixture was diluted with ether (10 mL) and filtered through a column of Florisil (3 g). The filtrate was concentrated, and the residue was subjected to chromatography (silica gel, 20 g; elution with 3:1 hexane–ether) to give crude aldehyde (201 mg). This material was purified by MPLC (elution with 24:1 hexane–AcOEt), providing homogeneous **11** (174 mg, 45%) as a colorless oil: $[\alpha]^{23}_D$ −1.49° (*c* 0.976, $CHCl_3$); R_f 0.59 (4:1 hexane–AcOEt); IR (neat) 1680 cm^{-1}; ^{1}H NMR (270 MHz) δ −0.01, 0.01 (each 3 H, s, $SiMe_2$), 0.86 (3 H, d, J = 6.8 Hz, Me-4), 0.89 (9 H, s, *t*-Bu), 1.02 (3 H, d, J = 6.6 Hz, Me-6), 1.12 (1 H, ddd, J = 15.1, 8.7, 6.7 Hz, H-5), 1.50–1.70 (2 H, m, H-5 and H-6), 1.76 (3 H, d, J = 1.2 Hz, Me-2), 1.77 (3 H, s, Me-12), 2.77 (1 H, m, H-4), 3.98 (1 H, dd, J = 6.8, 6.8 Hz, H-7), 4.17 (2 H, d, J = 6.8 Hz, H-14), 4.52 (2 H, s, OCH_2Ph), 5.64 (1 H, dd, J = 14.2, 6.8 Hz, H-8), 5.69 (1 H, br t, J = 6.8 Hz, H-13), 6.10–6.40 (3 H, m, H-9, H-10, and H-11), 6.30 (1 H, dd, J = 9.8, 1.2 Hz, H-3), 7.34 (5 H, m, Ar H), 9.39 (1 H, s, CHO); MS, m/e 496.3353 (M$^+$, calcd 496.3370), 481, 388, 357, 91 (base peak).

Compound 12. By the same procedure as described above for **11**, 817 mg (1.73 mmol) of the *O*-methoxymethyl derivative of **10** afforded **12** (225 mg, 31%) as a colorless oil: $[\alpha]^{23}_D$ −58.98 (*c* 1.272, $CHCl_3$); R_f 0.24 (7:1 hexane–AcOEt); IR (neat) 1685 cm^{-1}; ^{1}H NMR δ 0.91 (3 H, d, J = 6.8 Hz, Me-4), 1.04 (3 H, d, J = 6.6 Hz, Me-6), 1.10–1.30 (1 H, ddd, J = 14.0, 8.1, 6.8 Hz, H-5), 1.77 (3 H, d, J = 1.2 Hz, Me-12), 1.78 (3 H, d, J = 1.0 Hz, Me-2), 1.55–1.82 (2 H, m, H-5 and H-6), 2.82 (1 H, m, H-4), 3.34 (3 H, s, OCH_3), 3.88 (1 H, dd, J = 8.3, 5.6 Hz, H-7), 4.17 (2 H, d, J = 6.8 Hz, H-14), 4.49, 4.68 (each 1 H, d, J = 6.6 Hz, OCH_2O), 4.52 (2 H, s, OCH_2Ph), 5.53 (1 H, dd, J = 14.3, 8.3 Hz, H-8), 5.70 (1 H, td, J = 6.8, 1.2 Hz, H-13), 6.20–6.32 (4 H, m, H-3, H-9, H-10, and H-11), 7.35 (5 H, m, Ar H), 9.39 (1 H, s, CHO); MS, m/e 426.2732 (M$^+$, calcd 426.2769), 410, 381, 364, 318, 303, 135 (base peak).

(1*S*,2*S*,4a*S*,5*S*,6*S*,8*S*,8a*R*)- and (1*R*,2*R*,4a*R*,5*S*,6*S*,8*S*,8a*S*)-2-[3-(Benzyloxy)-1-methyl-1(*E*)-propenyl]-5-[(*tert*-butyldimethylsilyl)oxy]-1,6,8-trimethyl-1,2,4a,5,6,7,8,8a-octahydronaphthalene-1-carboxaldehyde (13

and 14). To a stirred solution of **11** (113 mg, 0.228 mmol) in dry CH_2Cl_2 (2.3 mL) cooled at ca. −80 °C was added a 1.0 M hexane solution of Me_2AlCl (0.23 mL) over 2 min. The solution was allowed to warm to −40 °C over 5.5 h and then diluted with CH_2Cl_2 (15 mL), and saturated aqueous $NaHCO_3$ (10 mL) was added. Phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (10 mL × 4). The combined organic phases were washed with brine (5 mL), dried, and concentrated. The residual oil was subjected to MPLC (elution with 24:1 hexane–AcOEt, relative t_R = 1.47) to give **14** (25 mg, 22%) and **13** (73 mg, 65%) in the order of elution.

Compound 13: colorless oil, slowly crytallized in a freezer as needles, mp 47–50 °C; $[\alpha]^{23}_D$ −92.99° (*c* 1.141, $CHCl_3$); R_f 0.59 (4:1 hexane–AcOEt); IR (KBr) 1720 cm^{-1}; ^1H NMR (270 MHz) δ 0.08, 0.10 (each 3 H, s, $SiMe_2$), 0.67 (3 H, d, *J* = 6.1 Hz, Me-8), 0.94 (9 H, s, *t*-Bu), 1.01 (3 H, d, *J* = 7.1 Hz, Me-6), 1.10 (3 H, s, Me-1), 1.35–1.70 (4 H, m, H-7ax, H-7eq, H-8, and H-8a), 1.63 (3 H, d, *J* = 1.1 Hz, Me-1′), 2.08 (2 H, m, H-6 and H-4a), 2.36 (1 H, m, H-2), 3.53 (1 H, dd, *J* = 10.5, 5.1 Hz, H-5), 4.01, 4.08 (each 1 H, dd, *J* = 12.8, 6.3 Hz, H-3′), 4.49 (2 H, s, OCH_2Ph), 5.43 (1 H, ddd, *J* = 10.3, 4.6, 2.7 Hz, H-3), 5.53 (1 H, ddd, *J* = 6.3, 6.3, 1.1 Hz, H-2′), 6.07 (1 H, ddd, *J* = 10.3, 1.7, 1.7 Hz, H-4), 7.33 (5 H, m, Ar H), 9.45 (1 H, s, CHO); ^1H NMR (400 MHz) (C_6D_6) δ 0.07, 0.13 (each 3 H, s, $SiMe_2$), 0.59 (3 H, d, *J* = 6.7 Hz, Me-8), 0.98 (3 H, d, *J* = 7.2 Hz, Me-6), 1.02 (9 H, s, *t*-Bu), 1.14 (3 H, s, Me-1), 1.10–1.19 (1 H, m, H-7ax), 1.27 (1 H, ddd, *J* = 13.6, 2.9, 2.6 Hz, H-7eq), 1.40–1.53 (1 H, m, H-8), 1.51 (3 H, d, *J* = 0.8 Hz, Me-1′), 1.66 (1 H, dd, *J* = 10.4, 10.4 Hz, H-8a), 1.98 (1 H, m, H-6), 2.10 (1 H, ddd, *J* = 10.4, 10.4, 2.3 Hz, H-4a), 2.35 (1 H, dd, *J* = 2.3, 2.3 Hz, H-2), 3.53 (1 H, dd, *J* = 10.4, 5.2 Hz, H-5), 3.90, 3.93 (each 1 H, dd, *J* = 10.5, 6.1 Hz, H-3′), 4.37 (2 H, s, CH_2OPh), 5.41 (1 H, ddd, *J* = 10.2, 4.9, 2.3 Hz, H-3), 5.67 (1 H, ddd, *J* = 6.1, 6.1, 0.8 Hz, H-2′), 6.19 (1 H, ddd, *J* = 10.2, 2.3, 2.3 Hz, H-4), 7.08–7.35 (5 H, m, Ar H), 9.57 (1 H, s, CHO); MS, *m/e* 496.3327 (M^+, calcd 496.3370), 439, 388, 357, 331, 55 (base peak). Anal. Calcd for $C_{31}H_{48}O_3Si$: C, 74.95; H, 9.74. Found: C, 74.94; H, 9.49.

Compound 14: colorless oil; $[\alpha]^{23}_D$ −122.76° (c 1.671, $CHCl_3$); R_f 0.59 (4:1 hexane–AcOEt); IR (neat) 1720 cm^{-1}; ^1H NMR (270 MHz) δ 0.06, 0.08 (each 3 H, s, $SiMe_2$), 0.70 (3 H, d, *J* = 6.6 Hz, Me-8), 0.90 (9 H, s, *t*-Bu), 0.99 (3 H, d, *J* = 7.3 Hz, Me-6), 1.09 (3 H, s, Me-1), 1.25 (1 H, br d, *J* = 12.5 Hz, H-7eq), 1.46–1.68 (1 H, m, H-8), 1.68 (3 H, s, Me-1′), 1.79 (1 H, ddd, *J* = 12.5, 12.5, 5.1 Hz, H-7ax), 1.88 (1 H, m, H-6), 2.12 (1 H, ddd, *J* = 10.5, 2.6, 2.0 Hz, H-4a), 2.32 (1 H, dd, *J* = 10.5, 10.5 Hz, H-8a), 2.42 (1 H, m, H-2), 3.74 (1 H, m, H-5), 3.97, 4.01 (each 1 H, dd, *J* = 12.3, 6.5 Hz, H-3′), 4.46 (2 H, s, OCH_2Ph), 5.43 (1 H, ddd, *J* = 10.0, 4.4, 2.7 Hz, H-3), 5.53 (1 H, br d, *J* = 10.0 Hz, H-4), 5.58 (1 H, dd, *J* = 6.5, 6.5 Hz, H-2′), 7.32 (5 H, m, Ar H), 9.47 (1 H, s, CHO); MS, *m/e* 496.3403 (M^+, calcd 496.3372), 439, 411, 331, 18 (base peak).

(1*S*,2*S*,4a*S*,5*S*,6*S*,8*S*,8a*R*)- and (1*R*,2*R*,4a*R*,5*S*,6*S*,8*S*,8a*S*)-2-[3-(Benzyloxy)-1-methyl-1(*E*)-propenyl]-5-(methoxymethoxy)-1,6,8-trimethyl-1,2,4a,5,6,7,8,8a-octahydronaphthalene-1-carboxaldehyde (15 and 16). To a stirred solution of **12** (83 mg, 0.194 mmol) in dry CH_2Cl_2 (1.9 mL) cooled at ca. −90 °C was added a 1.0 M hexane solution of Me_2AlCl (0.194 mL) over 1 min. The solution was allowed to warm to −40 °C over 20 min and then stirred for 8 h at −50 to −40 °C. The mixture was diluted with CH_2Cl_2 (10 mL), and saturated $NaHCO_3$ (10 mL) was added. Phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (10 mL × 4). The combined organic phases were washed with brine (5 mL), dried, and concentrated. The residual oil was subjected to MPLC (elution with 9:1 hexane–AcOEt, relative t_R (**15**/**16**) = 1.34) to give **16** (1 mg, 1%), **15** (33 mg, 40%), and recovered **12** (5 mg, 6%) in the order of elution.

Compound 15: colorless oil; $[\alpha]^{23}_D$ −117.72° (*c* 3.799, $CHCl_3$); R_f 0.29 (hexane–AcOEt, 7:1); IR (neat) 1720 cm^{-1}; ^1H NMR (270 MHz) δ 0.70 (3 H, d, *J* = 6.1 Hz, Me-8), 1.03 (3 H, d, *J* = 7.1 Hz, Me-6), 1.11 (3 H, s, Me-2), 1.35–1.73 (4 H, m, H-7ax, H-7eq, H-8, and H-8a), 1.64 (3 H, d, *J* = 1.0 Hz, Me-1′), 2.15 (1 H, tm, *J* = 10.1 Hz, H-4a), 2.32 (1 H, m, H-6), 2.43 (1 H, m, H-2), 3.43 (3 H, s, OCH_3), 3.47 (1 H, dd, *J* = 10.1, 5.1 Hz, H-5), 4.02, 4.06 (each 1 H, br dd, *J* = 12.5, 6.4 Hz, H-3′), 4.49 (2 H, s, OCH_2Ph), 4.68, 4.79 (each 1 H, d, *J* = 6.9 Hz, OCH_2O), 5.48 (1 H, ddd, *J* = 10.2, 4.6, 2.7 Hz, H-3), 5.53 (1 H, dt, *J* = 6.4, 1.0 Hz, H-2′), 6.03 (1 H, ddd, *J* = 10.2, 1.7, 1.7 Hz, H-4), 7.34 (5 H, m, Ar H), 9.45 (1 H, s, CHO); MS, *m/e* 426.2749 (M^+, calcd 426.2769), 410, 256, 135, 91 (base peak).

Compound 16: colorless oil, $[\alpha]^{23}_D$ −127.02° (*c* 0.151, $CHCl_3$); R_f 0.29 (hexane–AcOEt, 7:1); IR (neat) 1720 cm^{-1}; ^1H NMR (270 MHz) δ 0.70 (3 H, d, *J* = 6.4 Hz, Me-8), 1.02 (3 H, d, *J* = 7.3 Hz, Me-6), 1.10 (3 H, s, Me-1), 1.31 (1 H, br d, *J* = 12.9 Hz, H-7eq), 1.51–1.67 (1 H, m, H-8), 1.67 (3 H, s, Me-1′), 1.75 (1 H, ddd, *J* = 12.9, 12.9, 5.1 Hz, H-7ax), 2.07 (1 H, m, H-6), 2.18 (1 H, ddd, *J* = 10.5, 2.4, 2.4 Hz, H-4a), 2.38 (1 H, dd, *J* = 10.5, 10.5 Hz, H-8a), 2.41 (1 H, m, H-2), 3.37 (3 H, s, OCH_3), 3.66 (1 H, br s, H-5), 4.02, 4.08 (each 1 H, dd, *J* = 12.7, 6.2 Hz, H-3′), 4.49 (2 H, s, OCH_2Ph), 4.60, 4.72 (each 1 H, d, *J* = 7.1 Hz, OCH_2O), 5.49 (1 H, ddd, *J* = 10.0, 4.6, 2.4 Hz, H-3), 5.60 (1 H, br d, *J* = 10.0 Hz, H-4), 5.69 (1 H, br t, *J* = 6.2 Hz, H-2′), 7.33 (5 H, m, Ar H), 9.49 (1 H, s, CHO); MS, *m/e* 426.2789 (M^+, calcd 426.2769), 381, 364, 335, 319, 303, 91, 45 (base peak).

Registry No. 1, 78798-07-9; 4, 112572-86-8; 5, 79646-66-5; 6, 110715-33-8; 7, 101376-74-3; 8, 112505-65-4; 9, 112505-66-5; 9 (lactol), 112505-67-6; 10, 112505-68-7; 10 (R^2 = TBS), 112505-69-8; 10 (R^2 = MOM), 112505-72-3; 11, 112505-71-2; 11 (alcohol), 112505-70-1; 12, 112505-73-4; 13, 112505-75-6; 14, 112505-74-5; 15, 112505-77-8; 16, 112505-76-7; $(EtO)_2P(O)CH_2COMe$, 1067-74-9; (*E*,*E*)-$BnOCH_2CH{=}C(CH_3)CH{=}CHCOMe$, 112505-62-1; (*E*,*E*)-$BnOCH_2CH{=}C(CH_3)CH{=}CHCH_2OH$, 112505-63-2; (*E*,*E*)-$BnOCH_2CH{=}C(CH_3)CH{=}CHCH_2Br$, 112505-64-3; $Ph_3P{=}C(Me)CoOEt$, 5717-37-3; tetronolide, 76705-48-1.

Preparation of (*S*)-(−)-4-Methyl-2-cyclohexen-1-one: A Useful Chiral Building Block

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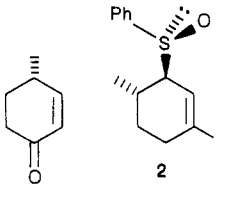
In the course of studies involving the enantioselective synthesis of trichothecenes[1] via chiral sulfinylallyl anions,[2] optically pure (*S*)-(−)-4-methyl-2-cyclohexen-1-one (**1**) was required as the starting material for the preparation of the chiral allylic sulfoxide **2**.[3] Barieux and Gore prepared



2

1

optically pure (*R*)-**1** from (*R*)-**3**-methylcyclohexanone by a sequence of reactions.[4] However, (*S*)-3-methylcyclohexanone, the starting material for (*S*)-**1**, is not commer-

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(2) (a) Hua, D. H.; Venkataraman, S.; Coulter, M. J.; Sinai, G.-Z. *J. Org. Chem.* **1987**, *52*, 719. (b) Hua, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 3835. (c) Hua, D. H.; Sinai, G.-Z.; Venkataraman, S. *J. Am. Chem. Soc.* **1985**, *107*, 4088.

(3) Hua, D. H.; Venkataraman, S.; Chan, Y.-K.-R.; Paukstelis, J. K. *J. Am. Chem. Soc.*, submitted for publication.

(4) Barieux, J.-J.; Gore, J. *Bull. Soc. Chim. Fr.* **1971**, 3978. (*R*)-**1** was prepared in five steps.

0022-3263/88/1953-1095$01.50/0