Electronic Supplementary Information

Two-directional synthesis and stereochemical assignment toward a C_2 symmetric oxasqualenoid (+)-intricatetraol

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Dibenzyl Ether 8. To a solution of sodium hydride (60% oil dispersion, 2.23 g, 55.7 mmol) in tetrahydrofuran (132 mL) was added dropwise a solution of diol **7**[3b] (2.66 g, 15.6 mmol) in tetrahydrofuran (24 mL) at 0 °C under a nitrogen atmosphere, and the solution was stirred at room temperature for 1 h. To the solution were added benzyl bromide (4.94 mL, 40.7 mmol) and tetrabutylammonium iodide (1.18 g, 3.13 mmol), and the solution was stirred under reflux for 18 h. After the solution was cooled to room temperature, water (200 mL) was added to the solution and the aqueous layer was extracted with ether (150 mL × 3). The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/ethyl acetate = 98:2 to 80:20) on 100 g of silica gel to give dibenzyl ether **8** (5.46 g, 100% yield) as a colorless oil: R_f = 0.85 (hexane/ethyl acetate = 50:50); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.24 (10H, m), 5.36 (2H, br s), 4.44 (4H, s), 3.99 (4H, s), 2.11–2.00 (4H, m), 1.78 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 132.6, 128.9, 128.3, 127.7, 127.5, 71.7, 68.5, 28.0, 21.6; IR (neat) 3064, 3031, 2917, 2856, 1496, 1454, 1366, 1252, 1203, 1070, 1028, 909, 733, 698, 648 cm^{-1}; FAB-MS *m/z* (relative intensity) 351.2 [$(M + H)^+$, 5.0], 135.1 (10), 91.0 (100); FAB-HRMS calcd for $C_{24}H_{31}O_2$ [$(M + H)^+$] 351.2324, found 351.2319.

Diol 11. To a solution of *tert*-butyl alcohol (55 mL) and water (65 mL) was added 16.5 g of AD-mix-β (1.4 g/1 mmol of the olefin) under a nitrogen atmosphere at room temperature, and stirring at the same temperature produced two clear phases. After the lower aqueous phase appeared bright yellow, methanesulfonamide (1.23 g, 13.0 mmol) was added to the solution. The mixture was cooled to 0 °C, whereupon some of the dissolved salts precipitated. A solution of diene **8** (2.07 g, 5.90 mmol) in 10 mL of *tert*-butyl alcohol was added to the mixture, and the heterogeneous slurry was stirred vigorously at 0 °C for 17 h. While the mixture was stirred at 0 °C, solid sodium sulfite (16.9 g, 134 mmol) was added and the mixture was allowed to warm to room temperature and stirred for 1 h. Ethyl acetate (100 mL) was added to the reaction mixture, and after separation of the layers, the aqueous phase was further extracted with the organic solvent (50 mL × 3). The combined organic layers were washed with a 2 N aqueous solution of potassium hydroxide, dried over anhydrous magnesium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/ethyl acetate = 30:70 to 20:80) on 40 g of silica gel to afford an inseparable mixture of diastereomeric tetraols **9** and **10** (2.47 g, 100% yield) as a colorless oil: R_f = 0.13 (hexane/ethyl acetate = 50:50).

To a solution of the diastereomeric tetraols **9** and **10** (3.79 g, 9.07 mmol) and 2,6-lutidine (5.24 mL, 45.3 mmol) in 60 mL of dichloromethane was added dropwise triisopropylsilyl triflate (7.31 mL, 27.2 mmol) at 0 °C under a nitrogen atmosphere, and the mixture was stirred at room temperature for 1 h. Water (60 mL) was added to the reaction mixture, and the aqueous layer was extracted with dichloromethane (40 mL × 3). The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/ethyl acetate =97:3) on 120 g of silica gel to provide C_2 symmetric diol **11** (4.44 g, 67.0% yield) and *meso* diol **12** (1.85 g, 27.9% yield) as each colorless oil.

Diol 11: R_f = 0.50 (hexane/ethyl acetate = 80:20); $[\alpha]_D^{26}$ +4.78 (*c* 1.03, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.24 (10H, m), 4.57 (2H, d, *J* = 12.0 Hz), 4.49 (2H, d, *J* = 11.7 Hz), 3.77 (2H, t, *J* = 5.0 Hz), 3.56 (2H, d, *J* = 9.0 Hz), 3.32 (2H, d, *J* = 9.0 Hz), 2.61 (2H, s), 1.96–1.80 (2H, m), 1.69–1.53 (2H, m), 1.15 (6H, s), 1.05 (42H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 128.3, 127.7, 127.6, 77.1, 75.1, 75.0, 73.4, 31.0, 20.1, 18.33, 18.31, 13.3; IR (neat) 3563, 2943, 2866, 1464, 1365, 1266, 1220, 1098, 1014, 883, 820, 739, 699, 679 cm^{-1}; FAB-MS *m/z* (relative intensity) 731.2 [(M +

H)$^+$, 2.0], 391.1 (7.0), 243.1 (17), 157.1 (16), 91.0 (100); FAB-HRMS calcd for $C_{42}H_{75}O_6Si_2$ [(M + H)$^+$] 731.5102, found 731.5101.

Diol 12: R_f = 0.42 (hexane/ethyl acetate = 80:20); $[\alpha]_D^{22}$ 0 (*c* 0.95, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.23 (10H, m), 4.56 (2H, d, *J* = 12.0 Hz), 4.48 (2H, d, *J* = 12.0 Hz), 3.82–3.72 (2H, m), 3.59 (2H, d, *J* = 8.8 Hz), 3.30 (2H, d, *J* = 8.8 Hz), 2.56 (2H, s), 2.00–1.89 (2H, m), 1.60–1.49 (2H, m), 1.14 (6H, s), 1.05 (42H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 128.3, 127.8, 127.6, 77.4, 75.0, 74.9, 73.4, 31.4, 19.7, 18.34, 18.32, 13.3; IR (neat) 3567, 2943, 2866, 1464, 1384, 1367, 1319, 1251, 1207, 1099, 1013, 883, 819, 734, 697, 678 cm^{-1}; FAB-MS *m/z* (relative intensity) 731.5 [(M + H)$^+$, 7.0], 391.3 (6.0), 243.3 (14), 157.2 (14), 91.0 (100); FAB-HRMS calcd for $C_{42}H_{75}O_6Si_2$ [(M + H)$^+$] 731.5103, found 731.5084.

Tetraol 13. A solution of palladium hydroxide on carbon (20%, 200 mg) and dibenzyl ether **11** (1.96 g, 2.68 mmol) in ethyl acetate (20 mL) was vigorously stirred at room temperature under a hydrogen atmosphere for 14 h. The reaction mixture was filtered through a pad of Celite, and the filtrates were concentrated under reduced pressure. The residue was purified by column chromatography (hexane/ethyl acetate = 30:70) on 30 g of silica gel to provide tetraol **13** (1.38 g, 93.6% yield) as a white solid: R_f = 0.48 (hexane/ethyl acetate = 50:50); mp 104.0–105.5°; $[\alpha]_D^{23}$ –4.08 (*c* 0.87, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (2H, t, *J* = 4.9 Hz), 3.77 (2H, dd, *J* = 11.0, 3.7 Hz), 3.43 (2H, dd, *J* = 10.9, 7.9 Hz), 2.80 (2H, s), 2.30 (2H, dd, *J* = 7.9, 3.8 Hz), 1.85–1.78 (2H, m), 1.74–1.67 (2H, m), 1.13 (6H, s), 1.11 (36H, s), 1.10 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 79.1, 74.9, 67.7, 31.4, 20.5, 18.27, 18.25, 13.2; IR (KBr) 3390, 2943, 2866, 1464, 1387, 1252, 1107, 1045, 1015, 999, 918, 883, 822, 681, 654 cm^{-1}; FAB-MS *m/z* (relative intensity) 551.3 [(M + H)$^+$, 17], 359.2 (21), 341.2 (15), 301.2 (15), 243.2 (17), 227.1 (35), 157.1 (100), 115.0 (94), 59.0 (92); FAB-HRMS calcd for $C_{28}H_{63}O_6Si_2$ [(M + H)$^+$] 551.4163, found 551.4140. Anal. Calcd for $C_{28}H_{62}O_6Si_2$: C, 61.04; H, 11.34. Found: C, 59.69; H, 11.18.

Di(*R*)-MTPA Ester 14. To a solution of tetraol **13** (22.0 mg, 39.9 μmol), 4-(*N*,*N*-dimethylamino)pyridine (30.0 mg, 0.240 mmol), and triethylamine (0.033 mL, 0.340 mmol) in 1 mL of dichloromethane was added (*S*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (0.022 mL, 0.120 mmol) at room temperature under a nitrogen atmosphere, and the mixture was then stirred for 14 h. Water (1 mL) was added to the reaction mixture, and the aqueous layer was extracted with dichloromethane (1 mL × 3). The organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The residue was subjected to column chromatography (hexane/ethyl acetate = 80:20) on 3 g of silica gel to provide di(*R*)-MTPA ester **14** (39.0 mg, 100% yield) as a colorless oil: R_f = 0.50 (hexane/ethyl acetate = 80:20); $[\alpha]_D^{25}$ +21.6 (*c* 0.58, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.57–7.51 (4H, m), 7.43–7.36 (6H, m), 4.38 (2H, d, *J* = 11.0 Hz), 4.32 (2H, d, *J* = 11.0 Hz), 3.71–3.66 (2H, m), 3.56 (6H, s), 2.20 (2H, s), 1.87–1.76 (2H, m), 1.60–1.51 (2H, m), 1.14 (6H, s), 1.06 (42H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 132.2, 129.7, 128.4, 127.4, 123.4 (q, *J* = 288.6 Hz), 84.8 (q, *J* = 27.3 Hz), 76.8, 75.2, 70.3, 55.5, 31.0, 19.9, 18.23, 18.20, 13.1; IR (neat) 3440, 2945, 2866, 1751, 1456, 1373, 1244, 1169, 1105, 1030, 1001, 916, 883, 822, 766, 719, 679 cm^{-1}; FAB-MS *m/z* (relative intensity) 982.9 $[(M + H)^+$, 7.0], 920.9 (7.0), 790.9 (24), 687.0 (13), 557.0 (52), 517.0 (47), 189.0 (100), 157.1 (30), 115.0 (47); FAB-HRMS calcd for $C_{48}H_{77}O_{10}F_6Si_2$ $[(M + H)^+]$ 983.4959, found 983.4965.

Diepoxide 15. To a solution of tetraol **13** (440 mg, 0.799 mmol) and pyridine (0.39 mL, 4.79 mmol) in 8 mL of dichloromethane was added dropwise methanesulfonyl chloride (0.19 mL, 2.40 mmol) at room temperature under a nitrogen atmosphere, and the mixture was stirred at the same temperature for 19 h. Water (10 mL) was added to the solution, and the aqueous layer was extracted with dichloromethane (10 mL × 3). The organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo* to afford the dimesylate which was taken to the next step without further purification.

To a solution of the above dimesylate in 8 mL of methanol was added potassium carbonate (440 mg, 3.19 mmol), and the mixture was stirred under a nitrogen atmosphere at room temperature for 2 h. Water (20 mL) was added to the reaction mixture, and the aqueous layer was extracted with dichloromethane (15 mL × 3). The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The residue was subjected to column chromatography (hexane/ethyl acetate = 100:0 to 90:10) on 13 g of silica gel to furnish diepoxide **15** (396 mg, 96.2% yield from the tetraol **13**) as a colorless oil: R_f = 0.33 (hexane/ethyl acetate = 90:10); $[\alpha]_D^{27}$ –14.0 (*c* 1.61, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 3.45–3.40 (2H, m), 2.70 (2H, d, *J* = 5.1 Hz), 2.57 (2H, d, *J* = 5.1 Hz), 1.85–1.65 (4H, m), 1.31 (6H, s), 1.06 (42H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 75.8, 58.4, 53.4, 30.5, 18.2, 18.1, 16.0, 12.7; IR (neat) 2945, 2868, 1464, 1373, 1313, 1248, 1117, 1086, 1069, 997, 972, 883, 822, 799, 677 cm^{-1}; FAB-MS *m/z* (relative intensity) 515.2 [$(M + H)^+$, 1.2], 513.2 [$(M - H)^+$, 0.9], 471.2 [(M – *i*-Pr)$^+$, 17], 227.2 (100), 213.2 (25), 157.1 (85), 115.0 (93), 73.0 (87), 59.0 (71); FAB-HRMS calcd for $C_{28}H_{59}O_4Si_2$ [$(M + H)^+$] 515.3952, found 515.3931; FAB-HRMS calcd for $C_{28}H_{57}O_4Si_2$ [$(M - H)^+$] 513.3795, found 513.3799; FAB-HRMS calcd for $C_{25}H_{51}O_4Si_2$ [(M – *i*-Pr)$^+$] 471.3326, found 471.3338.

Diol 16. To a solution of diepoxide **15** (1.21 g, 2.35 mmol) in 25 mL of tetrahydrofuran was added dropwise tetrabutylammonium fluoride (8.23 mL, 8.23 mmol, 1 M in tetrahydrofuran) at 0 °C under a nitrogen atmosphere, and the mixture was stirred at the same temperature for 1 h. Methanol (2 mL) was added to the solution, and the mixture was directly concentrated under reduced pressure. The residue was purified by column chromatography (chloroform/methanol = 100:0 to 30:1) on 30 g of silica gel to furnish diol **16** (474 mg, 100% yield) as a colorless oil: R_f = 0.33 (ethyl acetate); $[\alpha]_D^{26}$ +6.02 (*c* 0.78, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 3.63 (2H, d, *J* = 8.5 Hz), 2.89 (2H, d, *J* = 4.6 Hz), 2.70–2.55 (2H, br s), 2.63 (2H, d, *J* = 4.9 Hz), 1.93–1.82 (2H, m), 1.67–1.50 (2H, m), 1.36 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 71.9, 59.0, 50.7, 29.4, 17.8; IR (neat) 3400, 2993, 2968, 2930, 2891, 1448, 1429, 1391, 1346, 1300, 1238, 1196, 1153, 1109, 1061, 1026, 988, 955, 934, 916, 885, 820, 806, 773, 721 cm^{-1}; FAB-MS *m/z* (relative intensity) 203.1 [(M + H)$^+$, 17], 185.1 (18), 149.0 (32), 137.1 (31); FAB-HRMS calcd for $C_{10}H_{19}O_4$ [(M + H)$^+$] 203.1284, found 203.1283.

Diepoxide 5. To a solution of diol **16** (474 mg, 2.35 mmol) and *N*,*N*-diisopropylethylamine (16.2 mL, 94.0 mmol) in 25 mL of dichloromethane was added dropwise chloromethyl methyl ether (4.46 mL, 58.8 mmol) at 0 °C under a nitrogen atmosphere, and the mixture was then stirred at room temperature for 21 h. Water (50 mL) was added to the solution, and the aqueous layer was extracted with dichloromethane (30 mL × 3). The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/ethyl acetate = 75:25) on 40 g of silica gel to afford diepoxide **5** (644 mg, 94.4% yield) as a colorless oil: R_f = 0.78 (ethyl acetate); $[\alpha]_D^{26}$ +37.2 (*c* 0.51, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.74 (2H, d, *J* = 6.8 Hz), 4.58 (2H, d, *J* = 6.8 Hz), 3.38 (6H, s), 3.23–3.18 (2H, m), 2.78 (2H, d, *J* = 5.1 Hz), 2.63 (2H, d, *J* = 5.1 Hz), 1.88–1.68 (4H, m), 1.31 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 95.8, 79.2, 56.8, 55.6, 53.6, 27.7, 16.2; IR (neat) 2934, 2892, 1444, 1219, 1149, 1102, 1032, 953, 919, 823 cm^{-1}; FAB-MS *m/z* (relative intensity) 291 [(M + H)$^+$, 2.0], 289.1 (4.0), 197.1 (15), 167.1 (41), 154.0 (31), 137.1 (39), 73.0 (43), 45.0 (100); FAB-HRMS calcd for $C_{14}H_{27}O_6$ [(M + H)$^+$] 291.1808, found 291.1809.

Diol 4. To a solution of sulfide **6**[3f] (4.97 g, 15.5 mmol) and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (8.4 mL, 55.4 mmol) dissolved in 50 mL of tetrahydrofuran was added dropwise 8.9 mL (14.4 mmol) of *n*-butyllithium (1.6 M in hexane) under a nitrogen atmosphere at –78 °C, and the mixture was then stirred at 0 °C for 30 min. To the mixture was added dropwise a solution of diepoxide **5** (643 mg, 2.21 mmol) in 10 mL of tetrahydrofuran, and the mixture was stirred at 0 °C for 1 h. To the reaction mixture was added 50 mL of 1 M aqueous hydrochloric acid, and the aqueous layer was extracted with ether (50 mL × 3). The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The residue was subjected to column chromatography (hexane/ethyl acetate = 15:1 for sulfide **6** to 60:40 for the products) on 45 g of silica gel to yield recovered sulfide **6** (3.02 g, 60.8% yield) and the products (2.06 g, 100% yield) as a mixture of diastereomeric sulfides.

The above products (2.06 g, 2.21 mmol) was dissolved in a mixture of tetrahydrofuran (30 mL) and 2-propanol (15 mL) under a nitrogen atmosphere. Several pieces of metallic sodium (total 2.55 g, 111 mmol) was added portionwise to the boiling solution under reflux, and the resulting mixture was stirred under reflux for 7 h. After the mixture was cooled to room temperature, 50 mL of water was added to the solution and the mixture was extracted with ether (50 mL × 3). The organic layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated *in vacuo*. The residue was purified by column chromatography (hexane/ethyl acetate = 75:25 to 50:50) on 45 g of silica gel to give diol **4** (1.45 g, 91.3% yield from the diepoxide **5**) as a colorless oil: $R_f = 0.25$ (hexane/ethyl acetate = 60:40); $[\alpha]_D^{27}$ –3.42 (*c* 0.83, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.20 (2H, t, *J* = 6.6 Hz), 4.77 (2H, d, *J* = 6.8 Hz), 4.66 (2H, d, *J* = 6.6 Hz), 3.66 (2H, dd, *J* = 9.3, 3.4 Hz), 3.43 (6H, s), 3.31–3.23 (4H, m), 2.27–2.13 (4H, m), 2.13–1.97 (4H, m), 1.70–1.30 (12H, m), 1.64 (6H, s), 1.42 (6H, s), 1.33 (6H, s), 1.24 (6H, s), 1.13 (6H, s), 1.10 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 125.2, 106.4, 99.1, 90.3, 82.8, 80.1, 73.7, 55.9, 36.7, 36.1, 28.6, 28.1, 27.7, 26.8, 26.0, 23.5, 22.9, 21.7, 16.0; IR (neat) 3462, 2980, 2937, 1456, 1369, 1275, 1217, 1198, 1148, 1109, 1032, 1005, 914, 856, 754 cm^{-1}; FAB-MS *m/z* (relative intensity) 713.2 $[(M - H)^-$, 18], 589.2 (12), 571.2 (57), 363.1 (30), 297.0 (27), 222.9 (100), 220.9 (30), 148.9 (40); FAB-HRMS calcd for $C_{40}H_{73}O_{10}$ $[(M - H)^-]$ 713.5204, found 713.5189.

Diol 18. Diol **4** (1.45 g, 2.02 mmol) was dissolved in acetonitrile (13.5 mL) and dimethoxymethane (27 mL). To the solution were added ketone **17**[5] (1.57 g, 6.06 mmol), tetrabutylammonium hydrogen sulfate (103 mg, 0.303 mmol), and buffer (27 mL, 0.05 M solution of $Na_2B_4O_7\cdot 10H_2O$ in 4×10^{-4} M aqueous Na_2(EDTA)). A solution of Oxone (6.21 g, 10.1 mmol) in aqueous Na_2(EDTA) (4×10^{-4} M, 50 mL) and a solution of potassium carbonate (5.87 g, 42.4 mmol) in water (50 mL) were added dropwise separately to the solution at 0 °C over a period of 1.5 h via additional funnels, and the mixture was stirred at the same temperature for another 1 h. The reaction mixture was diluted with water (50 mL) and extracted with ether (100 mL × 3). The organic layer was washed with brine, dried over anhydrous potassium carbonate, and concentrated *in vacuo*. The residue was purified by flash column chromatography (hexane/ethyl acetate = 70:30 for ketone **17** to 0:100 for a mixture of products) on 50 g of silica gel to afford a mixture of products (diepoxide, monoTHF, and diTHF) as a colorless oil.

To a solution of the above mixture of products in 25 mL of dichloromethane was added (±)-10-camphorsulfonic acid (25 mg, 0.110 mmol), and the solution was stirred at 0 °C for 5 min. Triethylamine (0.1 mL) was added to the solution, and the resulting mixture was concentrated *in vacuo*. The residue was purified by flash column chromatography (hexane/ethyl acetate = 65:35) on 20 g of silica gel to provide diol **18** (754 mg, 50.0% yield form the diol **4**) as a colorless oil: R_f = 0.50 (hexane/ethyl acetate = 20:80); $[\alpha]_D^{24}$ +23.1 (*c* 1.01, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 4.77 (2H, d, *J* = 6.3 Hz), 4.69 (2H, d, *J* = 6.3 Hz), 3.83 (2H, t, *J* = 6.7 Hz), 3.69–3.61 (2H, m), 3.50–3.43 (2H, m), 3.39 (6H, s), 3.04 (2H, s), 2.15–1.85 (6H, m), 1.75–1.42 (14H, m), 1.42 (6H, s), 1.33 (6H, s), 1.26 (6H, s), 1.21 (6H, s), 1.16 (6H, s), 1.12 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.5, 98.3, 85.6, 84.2, 84.1, 83.9, 80.3, 73.1, 55.9, 35.3, 32.4, 28.6, 28.2, 26.9, 26.1, 25.3, 23.9, 23.2, 23.0, 22.9; IR (neat) 3460, 2974, 2932, 2882, 1456, 1364, 1340, 1271, 1198, 1032, 1001, 912, 854, 826, 802 cm^{-1}; FAB-MS *m/z* (relative intensity) 745.1 [$(M - H)^-$, 25], 297.1 (18), 148.0 (100), 146.0 (25); FAB-HRMS calcd for $C_{40}H_{73}O_{12}$ [$(M - H)^-$] 745.5102, found 745.5099.

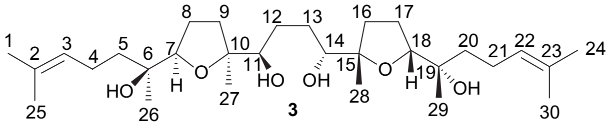
Bislactol 19. A solution of bisacetonide **18** (65.7 mg, 88 μmol) in 3.2 mL of acetic acid and 0.8 mL of water was stirred at room temperature for 66 h. The solution was concentrated under reduced pressure to give the hexaol which was taken to the next step without further purification.

To a solution of the above hexaol in 2.2 mL of dichloromethane and 2.2 mL of water was added a portion of sodium metaperiodate (88.1 mg, 0.412 mmol), and the mixture was vigorously stirred at room temperature for 17 h. A saturated aqueous solution of sodium sulfite (3 mL) was added to the solution, and the aqueous layer was extracted with dichloromethane (5 mL × 3). The organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The residue was purified by flash column chromatography (hexane/ethyl acetate = 50:50 to 0:100) on 5 g of silica gel to yield bislactol **19** (43.8 mg, 91.1% yield from the bisacetonide **18**) as a colorless oil: R_f = 0.35 (ethyl acetate); $[\alpha]_D^{25}$ +11.1 (*c* 0.29, $CHCl_3$); FAB-MS *m/z* (relative intensity) 545.3 [$(M - H)^-$, 10], 306.1 (33), 305.1 (32), 199.1 (25), 153.0 (100), 152.0 (53); FAB-HRMS calcd for $C_{28}H_{49}O_{10}$ [$(M - H)^-$] 545.3326, found 545.3319.

Diol 20. To a suspension of isopropyltriphenylphosphonium iodide (173 mg, 0.401 mmol) in 4 mL of tetrahydrofuran at –78 °C under a nitrogen atmosphere was added dropwise *n*-butyllithium (0.35 mL, 0.561 mmol, 1.6 M in hexane), and the solution was stirred at room temperature for 1 h. After the solution was cooled to –78 °C, a solution of bislactol **19** (43.8 mg, 80 μmol) in 2 mL of tetrahydrofuran was added dropwise to the solution. The solution was allowed to warm to room temperature and further stirred for additional 16 h. Water (10 mL) was added to the solution, and the aqueous layer was extacted with ether (10 mL × 3). The organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The residue was purified by flash column chromatography (hexane/ethyl acetate = 90:10 to 60:40) on 6 g of silica gel to provide diol **20** (30.4 mg, 63.4% yield) as a colorless oil: R_f = 0.53 (hexane/ethyl acetate = 50:50); $[\alpha]_D^{28}$ +29.0 (*c* 0.32, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.10 (2H, t, *J* = 7.1 Hz), 4.76 (2H, d, *J* = 6.6 Hz), 4.69 (2H, d, *J* = 6.6 Hz), 3.83 (2H, dd, *J* = 7.6, 6.1 Hz), 3.47–3.42 (2H, m), 3.38 (6H, s), 2.87 (2H, s), 2.14–1.82 (10H, m), 1.74–1.44 (8H, m), 1.68 (6H, s), 1.61 (6H, s), 1.34 (2H, ddd, *J* = 13.4, 11.7, 5.6 Hz), 1.20 (6H, s), 1.15 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.5, 124.6, 98.2, 85.5, 84.3, 83.8, 73.2, 55.9, 38.0, 32.6, 28.2, 25.7, 25.2, 24.1, 22.7, 22.2, 17.6; IR (neat) 3462, 2970, 2932, 2885, 1456, 1375, 1150, 1101, 1078, 1036, 953, 920 cm^{-1}; FAB-MS *m/z* (relative intensity) 597.3 [$(M - H)^-$, 7.0], 305.0 (28), 199.0 (23), 153.0 (100), 152.0 (51); FAB-HRMS calcd for $C_{34}H_{61}O_8$ [$(M - H)^-$] 597.4367, found 597.4379.

Synthetic (+)-Tetraol 3. To a solution of diMOM ether **20** (10.3 mg, 17.2 μmol) in 1 mL of methanol was added dropwise 12 N aqueous hydrochloric acid (0.03 mL, 0.36 mmol), and the solution was stirred at room temperature for 39 h. A saturated aqueous solution of sodium hydrogen carbonate (2 mL) was added to the solution, and the aqueous layer was extracted with dichloromethane (2 mL × 3). The organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The residue was purified by flash column chromatography (hexane/ethyl acetate = 70:30 to 40:60) on 3 g of silica gel to furnish synthetic (+)-tetraol **3** (5.7 mg, 64.9% yield) as a colorless oil: R_f = 0.63 (hexane/ethyl acetate = 20:80); $[\alpha]_D^{29}$ +11.5 (*c* 0.18, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.11 (2H, t, *J* = 7.2 Hz), 3.84 (2H, t, *J* = 7.3 Hz), 3.58 (2H, d, *J* = 10.2 Hz), 2.23–1.74 (12H, m), 1.69 (6H, s), 1.65–1.31 (8H, m), 1.62 (6H, s), 1.26 (6H, s), 1.16 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.0, 124.3, 86.1, 84.1, 77.7, 74.1, 38.3, 31.6, 29.5, 26.6, 25.7, 24.2, 24.1, 22.3, 17.7; IR (neat) 3308, 2970, 2926, 2856, 1456, 1375, 1092, 1078, 1024, 984, 953, 907, 802 cm^{-1}; FAB-MS *m/z* (relative intensity) 511.3 [$(M + H)^+$, 2.0], 281.0 (4.0), 263.2 (1.0), 211 (2.0), 147.1 (18), 135.1 (10), 111 (13), 109 (25), 85 (20), 71 (47), 69 (92), 55.0 (100), 43.0 (62); FAB-HRMS calcd for $C_{30}H_{55}O_6$ [$(M + H)^+$] 511.3999, found 511.4028.

Table 1. ^1H and ^{13}C NMR Data of Synthetic and Degradation Product **3** in $CDCl_3$



3

position	^{13}C δ		^1H δ (multiplicity, *J* Hz)	
	synthetic (100 MHz)	degradation[a] (67.9 MHz)	synthetic (400 MHz)	degradation[a] (270 MHz)
1, 24	25.7	25.7	1.69 (s)	1.69 (s)
2, 23	132.0	131.9		
3, 22	124.3	124.4	5.11 (t, 7.2)	5.11 (dd, 7.0, 7.0)
4, 21	22.3	22.3		
5, 20	38.3	38.4		
6, 19	74.1	74.0		
7, 18	84.1	84.1	3.84 (t, 7.3)	3.84 (dd, 7.3, 7.3)
8, 17	26.6	26.5		
9, 16	31.6	31.7		
10, 15	86.1	86.1		
11, 14	77.7	77.7	3.58 (d, 10.2)	3.58 (br d, 9.9)
12, 13	29.5	29.5		
25, 30	17.7	17.7	1.62 (s)	1.62 (s)
26, 29	24.2	24.2	1.26 (s)	1.26 (s)
27, 28	24.1	24.0	1.16 (s)	1.16 (s)

[a] Cited from ref 2.