Synthesis of (−)-Tarchonanthuslactone, a *syn*-1,3-Polyol-Derived α,β-Unsaturated δ-Lactone

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The coupling reaction of the chiral building block (2) with the chiral epoxide (3) and highly *syn*-1,3-stereoselective reduction of the resulting β-hydroxy ketone (5) allowed us to achieve the stereoselective synthesis of tarchonanthuslactone (1).

Keywords 1,3-polyol; 1,3-asymmetric reduction; tarchonanthuslactone; methyl (3*R*,5*R*,7*R*)-3,5,7-trihydroxyoctanoate; α,β-unsaturated δ-lactone; *Tarchonanthus trilobus*

A 1,3-polyhydroxylated chain is often found as the backbone of biologically important polyene macrolides produced by microorganisms.[1] Higher plants produce several α,β-unsaturated δ-lactones[2] which seem to have originated biogenetically from the corresponding 1,3-polyhydroxylated acids. One of the members of this group is tarchonanthuslactone (**1**), which was isolated from *Tarchonanthus trilobus* (Compositae).[3] Its absolute configuration was established by synthesis.[4]

Recently, we have developed a general method for preparing all-*syn*-1,3-polyols where lithium aluminum hydride–lithium iodide reduction played an important role for the construction of *syn*-1,3-diol units with excellent *syn*-selectivity.[5] We report here a stereoselective synthesis of (−)-tarchonanthuslactone (**1**) based on this method. A key feature of our synthesis is the stereocontrolled formation of optically active (3*R*,5*R*,7*R*)-3,5,7-trihydroxyoctanoic acid (B) or its equivalent, which could be prepared from a

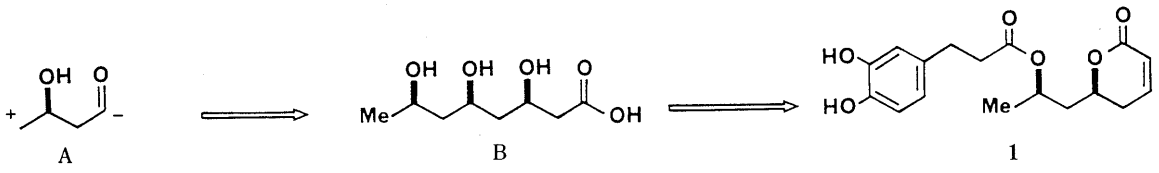

Chart 1

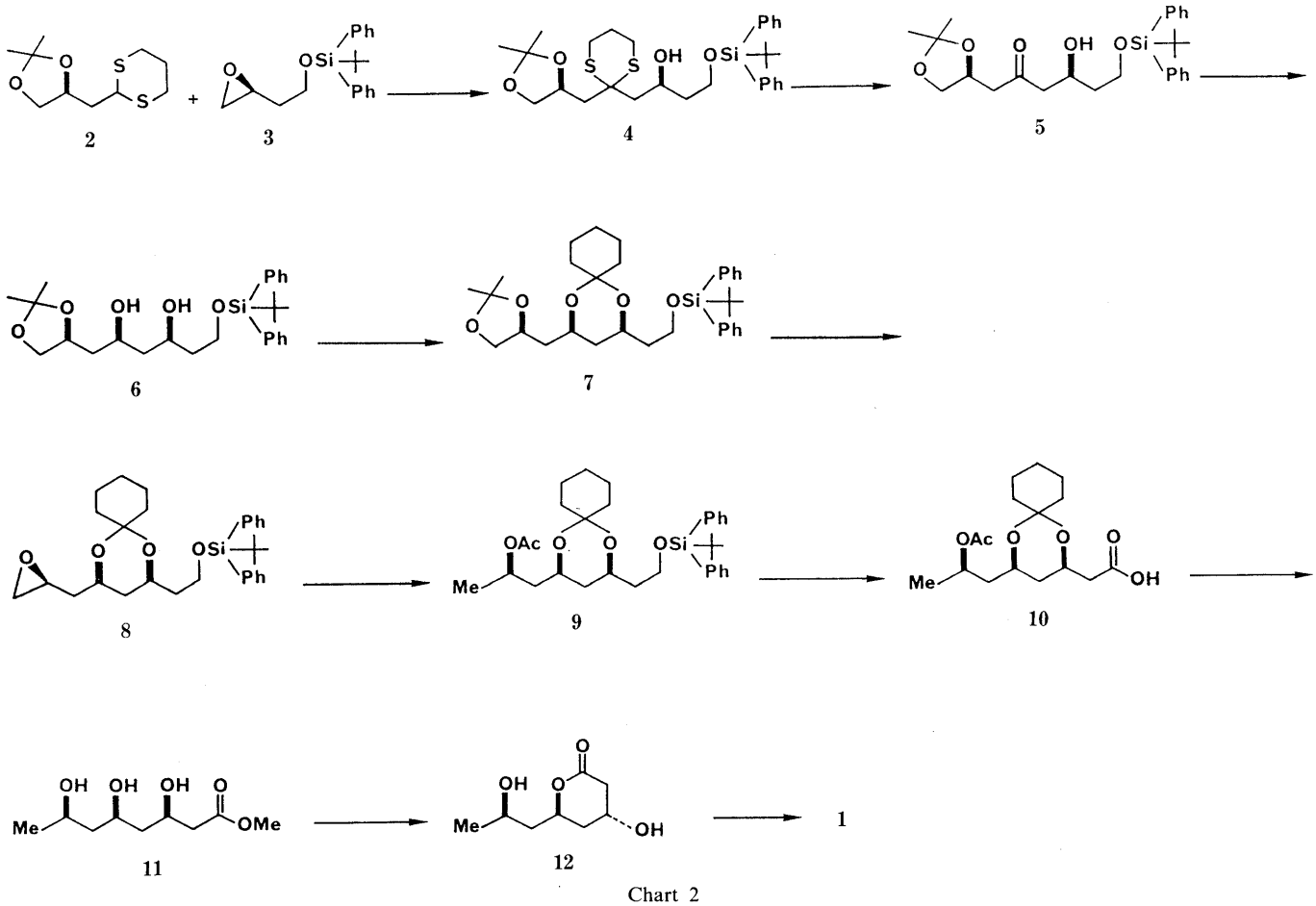

Chart 2

C_4 chiral unit (A).

Our synthesis of tarchonanthuslactone (**1**) started with the coupling reaction of the anion generated from the chiral dithiane (**2**), an equivalent to the C_4 unit (A), with the chiral epoxide (**3**) to give the adduct (**4**), which was converted to the hydroxy ketone (**5**) in 87% overall yield by treatment with methyl iodide–calcium carbonate in aqueous acetonitrile. A highly *syn*-stereoselective 1,3-asymmetric reduction was carried out using lithium aluminum hydride–lithium iodide in ether at $-100\,^{\circ}C$, providing the desired *syn*-diol (**6**) in 91% yield (*syn*:*anti*=95:5). The diastereoisomers are readily separable by flash chromatography. Protection of the *syn*-diol (**6**) with 1,1-dimethoxycyclohexane gave **7** (93%). The acetonide group of **7** was selectively deprotected with 80% acetic acid at $-5\,^{\circ}C$ in 42% yield (89% based on the consumed starting material) and the resulting 1,2-diol derivative was converted to the epoxide (**8**) in 78% overall yield by tosylation of the primary hydroxy group followed by base treatment.

Reduction of **8** with lithium aluminum hydride and then acetylation gave **9** which was transformed to the acid (**10**) (74%) by desilylation and oxidation with Jones reagent. Treatment of the acid with lithium methoxide in methanol and then Amberlyst-15 in one pot gave an 80% yield of all-*syn*-3,5,7-trihydroxy methyl ester (**11**). This ester is a key synthetic intermediate of tarchonanthuslactone (**1**) (Chart 1).

Cyclization of **11** to the lactone (**12**) was achieved with camphorsulfonic acid in methylene chloride in 60% yield (96% yield based on the consumed starting material). Completion of the synthesis required three more steps; i) diesterification of **12** with 3,4-dihydroxyhydrocinnamic acid protected with *tert*-butyldimethylsilyl group using dicyclohexylcarbodiimide (DCC), ii) formation of an α,β-unsaturated lactone by treatment with 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) in benzene, and iii) deprotection of the silyl group by tetra-*n*-butylammonium fluoride in the presence of benzoic acid in tetrahydrofuran, yielding (−)-tarchonanthuslactone (**1**), $[\alpha]_D^{23}$ -74.6° ($c=0.4$, $CHCl_3$), lit.,[3] $[\alpha]_D$ -67.2° ($c=2.3$, $CHCl_3$), in 87% overall yield. The spectral data (400 MHz ^{1}H-nuclear magnetic resonance (^{1}H-NMR), infrared (IR), mass spectra (MS)) were identical with the reported values.[3]

Experimental

Optical rotations were measured on a JASCO DIP-181 digital polarimeter. IR spectra were taken on a Hitachi 215 spectrometer. ^{1}H-NMR spectra were measured on a JEOL GX-400 spectrometer; chemical shifts are given in ppm with tetramethylsilane as an internal standard. MS were taken on Shimadzu GCMS QP-1000 and Hitachi M-80 mass spectrometers. Flash chromatography was performed with Silica gel 60 (230—400 mesh).

(2*S*,6*S*)-8-(*O*-*tert*-Butyldiphenylsilyl)-1,2-(*O*-isopropylidene)-4-(trimethylenedithio)octane-1,2,6,8-tetrol (4) A stirred solution of **2** (306 mg, 1.31 mmol) in 2 ml of dry tetrahydrofuran (THF) under nitrogen was treated with 0.86 ml of 1.6 M BuLi in hexane at $-40\,^{\circ}C$. The solution was stirred at $-30\,^{\circ}C$ for 2 h and then a solution of **3** (90 mg, 0.28 mmol) in 1 ml of dry THF was added. The reaction vessel was closed under positive pressure of nitrogen and stored at $-20\,^{\circ}C$ for 17 h. The reaction was quenched with aqueous NH_4Cl and the mixture was extracted with ether. The extract was washed with water and brine, dried ($MgSO_4$), and evaporated to dryness. Flash chromatography of the residue with ethyl acetate (EtOAc)–hexane (2:8) gave **4** (150 mg, 97% yield) as a colorless oil. $[\alpha]_D^{22}$ $+12.76^{\circ}$ ($c=0.7$, $CHCl_3$). IR (film): 3470, 1585, 1423, 1375, 1365, 1108, 820, 735, 700, 685 cm^{-1}. NMR ($CDCl_3$) δ: 1.06 (9H, s), 1.33 (3H, s), 1.36 (3H, s), 1.76 (2H, m), 1.93 (1H, m), 2.01 (1H, m), 2.11 (1H, dd, $J=15.2$, 1.7 Hz), 2.24 (1H, dd, $J=14.9$, 4.6 Hz), 2.32 (1H, dd, $J=14.9$, 6.4 Hz), 2.33 (1H, dd, $J=15.2$, 8.5 Hz), 2.74—3.01 (4H), 3.47 (1H, d, $J=2.2$ Hz, OH), 3.55 (1H, t, $J=8.0$ Hz), 3.85 (2H, t, $J=6.1$ Hz), 4.14 (1H, dd, $J=8.0$, 5.9 Hz), 4.26 (1H, m), 4.42 (1H, m), 7.37—7.45 (6H), 7.67—7.70 (4H). SIMS *m/z*: 561 (MH^+).

(2*S*,6*S*)-8-(*O*-*tert*-Butyldiphenylsilyl)-1,2-(*O*-isopropylidene)-octan-4-one-1,2,6,8-tetrol (5) A mixture of **4** (110 mg), $CaCO_3$ (49 mg), and CH_3I (0.5 ml) in 11 ml of 80% aqueous CH_3CN was stirred for 24 h at room temperature. The mixture was diluted with EtOAc (20 ml) and filtered through a short column of Celite. The filtrate was concentrated to dryness and the residue was flash-chromatographed with EtOAc–hexane (1:3) to give **5** (83 mg, 90% yield) as a colorless oil. $[\alpha]_D^{24}$ $+18.33^{\circ}$ ($c=0.3$, $CHCl_3$). IR (film): 3450, 1705, 1582 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.05 (9H, s), 1.35 (3H, s), 1.41 (3H, s), 1.68 (1H, m), 1.74 (1H, m), 2.59 (1H, dd, $J=16.6$, 4.2 Hz), 2.62 (1H, dd, $J=16.9$, 6.8 Hz), 2.68 (1H, dd, $J=16.6$, 8.1 Hz), 2.92 (1H, dd, $J=16.9$, 6.4 Hz), 3.45 (1H, d, $J=2.9$ Hz, OH), 3.55 (1H, dd, $J=8.3$, 6.8 Hz), 3.84 (2H, m), 4.18 (1H, dd, $J=8.3$, 6.1 Hz), 4.35 (1H, m), 4.48 (1H, quintet, $J=6.6$ Hz), 7.30—7.47 (6H), 7.52—7.68 (4H). SIMS *m/z*: 471 (MH^+).

(2*S*,4*S*,6*S*)-8-(*O*-*tert*-Butyldiphenylsilyl)-1,2-(*O*-isopropylidene)octane-1,2,4,6,8-pentol (6) A solution of **5** (193 mg, 0.41 mmol) and LiI (274 mg, 2.05 mmol) in 20 ml of dry ether under nitrogen was cooled to $-100\,^{\circ}C$ and $LiAlH_4$ (150 mg, 4.1 mmol) was added. The reaction mixture was stirred for 1 h at the same temperature under nitrogen and quenched with methanol (1 ml) and 2 N KOH (1 ml). After being stirred for 30 min at room temperature, the ethereal layer was separated and evaporated to dryness. The residue was flash-chromatographed with acetone–$CHCl_3$ (4:96) to give **6** (175 mg, 91% yield) as a colorless oil. $[\alpha]_D^{25}$ $+6.47^{\circ}$ ($c=0.34$, $CHCl_3$). IR ($CHCl_3$): 3480 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.05 (9H, s), 1.37 (3H, s), 1.43 (3H, s), 1.53—1.82 (6H), 3.59 (1H, dd, $J=8.1$, 7.6 Hz), 3.87 (2H, m), 3.98 (2H, OH), 4.08 (1H, m), 4.12 (1H, dd, $J=8.1$, 6.1 Hz), 4.16 (1H, m), 4.30 (1H, m), 7.38—7.46 (6H), 7.66—7.69 (4H). SIMS *m/z*: 473 (MH^+).

(2*S*,4*S*,6*S*)-8-(*O*-*tert*-Butyldiphenylsilyl)-4,6-(*O*-cyclohexylidene)-1,2-(*O*-isopropylidene)octane-1,2,4,6,8-pentol (7) A mixture of **6** (298 mg), 1,1-dimethoxycyclohexane (1 ml), and pyridinium *p*-toluenesulfonate (15 mg) in 3 ml of CH_2Cl_2 was stirred for 4 h at room temperature. After addition of triethylamine (0.5 ml) the mixture was evaporated to dryness. Flash chromatography with EtOAc–hexane (5:95) gave **7** (324 mg, 93% yield) as a colorless oil. $[\alpha]_D^{23}$ $+2.84^{\circ}$ ($c=0.9$, $CHCl_3$). IR (film): 1587, 1425, 1365, 1243, 1160, 1112, 968, 822, 720, 690 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.05 (9H, s), 1.21 (1H, dt, $J=12.7$, 11.7 Hz), 1.48 (1H, ddd, $J=12.7$, 2.7, 2.4 Hz), 1.62 (1H, ddd, $J=13.7$, 6.8, 5.4 Hz), 1.68 (2H, m), 1.92 (1H, dt, $J=13.7$, 6.8 Hz), 3.61 (1H, t, $J=7.8$ Hz), 3.71 (1H, dt, $J=10.3$, 5.1 Hz), 3.86 (1H, ddd, $J=10.3$, 7.6, 5.6 Hz), 3.98 (1H, m), 4.06 (1H, dd, $J=8.1$, 5.7 Hz), 4.14 (1H, m), 4.25 (1H, m), 7.35—7.44 (6H), 7.64—7.68 (4H). SIMS *m/z*: 553 (MH^+).

(2*S*,4*S*,6*S*)-8-(*O*-*tert*-Butyldiphenylsilyl)-4,6-(*O*-cyclohexylidene)-1,2-epoxyoctane-4,6,8-triol (8) A solution of **7** (290 mg) in 80% acetic acid (6 ml)–THF (0.6 ml) was allowed to stand at $-5\,^{\circ}C$ for 48 h. The reaction mixture was diluted with EtOAc, made alkaline with 28% NH_4OH under ice-water cooling, and extracted with EtOAc. The extract was washed with water and brine, dried ($MgSO_4$), and evaporated to dryness. Flash chromatography with EtOAc–hexane (4:6) gave the starting material (**7**) (154 mg) and a 1,2-diol compound (113 mg, 42% yield; 89% yield based on the consumed starting material).

The 1,2-diol compound (113 mg) was dissolved in pyridine (1 ml) and *p*-toluenesulfonyl chloride (210 mg) was added at 0 °C under stirring. The mixture was stirred for 3 h and extracted with ether. The extract was washed with water and brine, dried ($MgSO_4$), and evaporated to dryness. Flash chromatography with EtOAc–hexane (18:82) gave a monotosylate (122 mg, 83% yield).

A solution of the tosylate (112 mg) in ether (8 ml)–methanol (2 ml) was treated with excess KH at 0 °C. The mixture was stirred at 0 °C for 1 h and extracted with ether. The extract was washed with water and brine, dried ($MgSO_4$), and evaporated to dryness. Flash chromatography with EtOAc–hexane (1:9) gave the epoxide (**8**) (91 mg, 94% yield) as a colorless oil. $[\alpha]_D^{24}$ -1.93° ($c=1.0$, $CHCl_3$), IR ($CHCl_3$): 1422, 1200, 1108, 962, 818, 698 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.05 (9H, s), 2.53 (1H, dd, $J=5.1$, 2.7 Hz), 2.76 (1H, dd, $J=5.1$, 4.4 Hz), 3.06 (1H, m), 3.72 (1H, dt, $J=10.3$, 5.1 Hz), 3.87 (1H, ddd, $J=10.3$, 8.1, 5.4 Hz), 4.04 (1H, m), 4.15 (1H, m), 7.35—7.45 (6H), 7.65—7.69 (4H). HREIMS *m/z*: Calcd for $C_{30}H_{42}O_4Si$: 494.2769. Found: 494.2859.

(3*S*,5*R*,7*R*)-7-Acetoxy-1-(*O*-*tert*-butyldiphenylsilyl)-3,5-(*O*-cyclohexylidene)octane-1,3,5-triol (9) The epoxide (**8**) (31 mg) was dissolved in dry

ether (3 ml) and $LiAlH_4$ (10 mg) was added. The reaction mixture was stirred for 30 min at room temperature and quenched with 5 drops of 2 N KOH. Stirring was continued until precipitates formed. After filtration of the mixture through a short alumina column the filtrate was concentrated to dryness, giving an alcohol (29 mg, 95% yield).

The alcohol (29 mg) was dissolved in pyridine (0.5 ml) and acetic anhydride (0.5 ml) and stirred for 6 h at room temperature. After removal of the solvents *in vacuo* the residue was flash-chromatographed with EtOAc–hexane (8 : 92) to give **9** (31 mg, 98% yield) as a colorless oil. $[\alpha]_D^{23}$ $-3.31°$ ($c=1.55$, $CHCl_3$). IR ($CHCl_3$): 1725, 1425, 1370, 1254, 1108, 965, 695 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.05 (9H, s), 1.25 (3H, d, $J=6.4$ Hz), 2.03 (3H, s), 3.70 (1H, dt, $J=10.4$, 5.3 Hz), 3.82—4.0 (2H, m), 4.11 (1H, m), 5.09 (1H, sextet, $J=6.4$ Hz), 7.35—7.45 (6H), 7.64—7.69 (4H). HREIMS *m/z*: Calcd for $C_{32}H_{46}O_5Si$: 538.3095. Found: 538.3103.

(3*R*,5*R*,7*R*)-7-Acetoxy-3,5-(*O*-cyclohexylidene)-3,5-dihydroxyoctanoic acid (10) A solutionof **9** (30 mg, 0.056 mmol) in dry THF (2 ml) was treated with 1 M Bu_4NF in THF (0.18 ml) and the mixture was stirred for 2.5 h at room temperature. After removal of the solvent *in vacuo* the residue was flash-chromatographed with EtOAc–hexane (45 : 55) to give an alcohol (16 mg, 95% yield).

The alcohol (14 mg) was dissolved in acetone (1 ml) and excess Jones reagent was added at 0 °C. The mixture was stirred at 0 °C for 15 min and extracted with EtOAc. The extract was washed with water and brine, dried ($MgSO_4$), and evaporated to dryness. Flash chromatography with EtOAc–hexane (4 : 6) gave **10** (11.4 mg, 78% yield) as a colorless oil. $[\alpha]_D^{23}$ $+4.26°$ ($c=0.95$, $CHCl_3$). IR ($CHCl_3$): 3300—2700, 1715, 1372, 1250, 960 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.25 (3H, d, $J=6.4$ Hz), 2.03 (3H, s), 2.50 (1H, dd, $J=15.8$, 5.0 Hz), 2.57 (1H, dd, $J=15.8$, 7.1 Hz), 3.99 (1H, m), 4.31 (1H, m), 5.09 (1H, sextet, $J=6.4$ Hz). HREIMS *m/z*: Calcd for $C_{16}H_{26}O_6$: 314.1693. Found: 314.1710.

Methyl (3*R*,5*R*,7*R*)-3,5,7-Trihydroxyoctanoate (11) The acid (**10**) (35 mg) was dissolved in 3 ml of 0.1 N lithium methoxide in methanol and the solution was allowed to stand for 3.5 h at room temperature. The solution was diluted with 3 ml of methanol and Amberlyst-15 (400 mg) was added. The mixture was allowed to stand for 12 h and then filtered. The filtrate was concentrated to dryness to give the methyl ester (**11**) (20.3 mg, 88% yield) as a colorless oil. $[\alpha]_D^{22}$ $-29.32°$ ($c=1.0$, $CHCl_3$). IR ($CHCl_3$): 3475, 1720, 1434, 1142, 840 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.20 (3H, d, $J=7.4$ Hz), 1.50—1.76 (4H), 2.50 (2H, m), 3.72 (3H, s), 4.08 (1H, m), 4.16 (1H, m), 4.30 (1H, m). CIMS (NH_3) *m/z*: 207 (MH^+).

(3*R*,5*R*,7*R*)-3,5,7-Trihydroxyoctanoic Acid δ-Lactone (12) A solution of **11** (15 mg) and camphorsulfonic acid (1 mg) in 4 ml of CH_2Cl_2 was allowed to stand for 15 h at room temperature. After evaporation of the solvent the residue was flash-chromatographed with methanol–EtOAc (2 : 98) to give the starting material (**11**) (5.7 mg) and the lactone (**12**) (7.5 mg, 60% yield; 96% yield based on the consumed starting material) as a colorless oil. $[\alpha]_D^{21}$ $+19.9°$ ($c=0.48$, $CHCl_3$). IR ($CHCl_3$): 3400, 1725, 1268, 1078 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.26 (3H, d, $J=6.4$ Hz), 1.70 (1H, ddd, $J=14.2$, 5.1, 3.9 Hz), 1.79 (1H, ddd, $J=14.6$, 11.5, 2.9 Hz), 1.94 (1H, dt, $J=14.2$, 8.1 Hz), 2.03 (1H, br d, $J=14.6$ Hz), 2.65 (1H, ddd, $J=17.9$, 3.4, 1.7 Hz), 2.73 (1H, dd, $J=17.9$, 4.9 Hz), 4.08 (1H, m), 4.39 (1H, quintet, $J=3.4$ Hz), 4.94 (1H, m). CIMS (NH_3) *m/z*: 192 ($M+NH_4^+$).

Tarchonanthuslactone (1) (i) Diesterification of 12 The lactone (**12**) (5.7 mg) was dissolved in 2 ml of CH_2Cl_2 and 3,4-bis(*O*-*tert*-butyldimethylsilyl)-3,4-dihydroxyhydrocinnamic acid (40.3 mg), DCC (33.7 mg), and 4-dimethylaminopyridine (4 mg) were added successively. The mixture was stirred for 14 h at room temperature and filtered to remove precipitates. The filtrate was concentrated and the residue was flash-chromatographed with EtOAc–hexane (15 : 85) to give a diester (29.7 mg, 95% yield) as a colorless oil. $[\alpha]_D^{21}$ $-0.44°$ ($c=1.0$, $CHCl_3$). IR ($CHCl_3$): 1725, 1305, 1250, 900, 835 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.18 (24H, s), 0.97 (18H, s), 0.98 (18H, s), 1.24 (3H, d, $J=6.4$ Hz), 1.73 (2H, m), 2.06 (2H, m), 2.50—2.84 (10H), 4.56 (1H, m), 5.13 (1H, m), 5.22 (1H, m), 6.58—6.75 (6H). SIMS *m/z*: 959 (MH^+).

(ii) DBU Treatment of the Diester The diester (29.5 mg) was dissolved in 1 ml of benzene and 0.01 ml of DBU was added. After 10 min at room temperature the mixture was extracted with EtOAc. The extract was washed with 0.1% HCl and brine, dried ($MgSO_4$), and evaporated to dryness. Flash chromatography with EtOAc–hexane (1 : 3) gave an α,β-unsaturated δ-lactone (5.9 mg, 94% yield) as a colorless oil. $[\alpha]_D^{20}$ $-47.86°$ ($c=0.5$, $CHCl_3$). IR ($CHCl_3$): 1723, 1505, 1255, 900, 840 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.18 (6H, s), 0.19 (6H, s), 0.98 (9H, s), 0.99 (9H, s), 1.26 (3H, d, $J=6.4$ Hz), 1.81 (1H, ddd, $J=14.4$, 6.8, 4.4 Hz), 2.16 (1H, ddd, $J=14.4$, 8.3, 6.7 Hz), 2.21—2.41 (2H, m), 2.56 (2H, t, $J=7.5$ Hz), 2.81 (2H, t, $J=7.5$ Hz), 4.43 (1H, m), 5.10 (1H, m), 6.00 (1H, dd, $J=9.7$, 2.4 Hz), 6.62 (1H, dd, $J=8.1$, 2.0 Hz), 6.65 (1H, d, $J=2.0$ Hz), 6.70 (1H, d, $J=8.1$ Hz), 6.84 (1H, ddd, $J=9.0$, 5.9, 2.2 Hz). CIMS (NH_3) *m/z*: 566 ($M+NH_4^+$).

(iii) Tarchonanthuslactone (1) The unsaturated lactone (5.8 mg) obtained above was dissolved in 0.5 ml of dry THF and to this solution, benzoic acid (3.9 mg) and 1 M Bu_4NF in THF (26 μl) were added. The mixture was stirred for 20 min at room temperature and extracted with EtOAc. The extract was washed with water and brine, dried ($MgSO_4$), and evaporated to dryness. Flash chromatography with methanol–$CHCl_3$ (1.5 : 98.5) gave tarchonanthuslactone (**1**) (3.3 mg, 98% yield) as a colorless oil. $[\alpha]_D^{23}$ $-74.6°$ ($c=0.4$, $CHCl_3$). IR ($CHCl_3$): 3600—3200, 1720, 1600, 1520, 1445, 1380, 1260, 1040 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.25 (3H, d, $J=6.4$ Hz), 1.76 (1H, ddd, $J=14.7$, 7.1, 3.9 Hz), 2.07 (1H, ddd, $J=14.7$, 8.6, 6.1 Hz), 2.19 (1H, ddt, $J=18.3$, 11.7, 2.6 Hz), 2.35 (1H, dddd, $J=18.3$, 5.9, 3.9, 1.0 Hz), 2.61 (2H, t, $J=7.1$ Hz), 2.84 (2H, t, $J=7.1$ Hz), 4.16 (1H, dddd, $J=13.2$, 11.2, 6.1, 3.9 Hz), 5.06 (1H, ddq, $J=8.6$, 3.9, 6.4 Hz), 6.00 1H, ddd, $J=9.8$, 2.7, 1.0 Hz), 6.60 (1H, dd, $J=8.1$, 2.2 Hz), 6.73 (1H, d, $J=2.2$ Hz), 6.75 (1H, d, $J=8.1$ Hz), 6.84 (1H, ddd, $J=9.8$, 6.1, 2.4 Hz). HREIMS *m/z*: Calcd for $C_{17}H_{20}O_6$: 320.1234. Found: 320.1246.

Acknowledgment We thank Dr. T. Oishi, The Institute of Physical Chemical Research, for providing the ^{1}H-NMR spectrum of tarchonanthuslactone.

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