

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 -lactones² 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

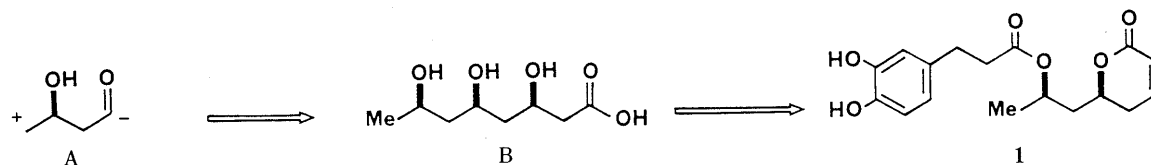


Chart 1

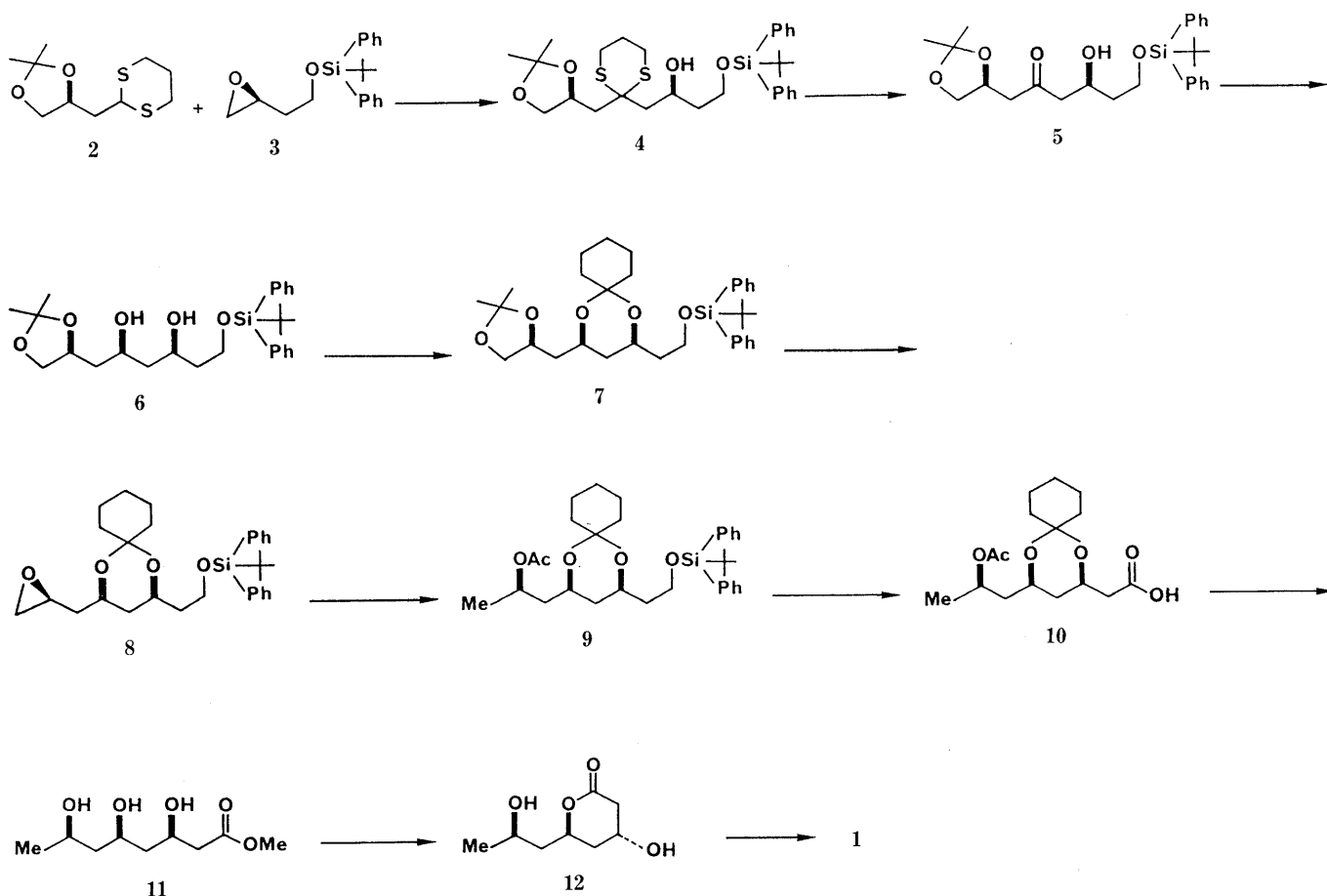


Chart 2

C₄ 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 C₄ 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°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°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**), $[\alpha]_{\text{D}}^{23} -74.6^{\circ}$ ($c=0.4$, CHCl_3), lit.,³⁾ $[\alpha]_{\text{D}} -67.2^{\circ}$ ($c=2.3$, CHCl_3), in 87% overall yield. The spectral data (400 MHz ¹H-nuclear magnetic resonance (¹H-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. ¹H-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).

(2S,6S)-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°C . The solution was stirred at -30°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°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. $[\alpha]_{\text{D}}^{22} +12.76^{\circ}$ ($c=0.7$, 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^+).

(2S,6S)-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. $[\alpha]_{\text{D}}^{24} +18.33^{\circ}$ ($c=0.3$, CHCl_3). IR (film): 3450, 1705, 1582 cm^{-1} . ¹H-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^+).

(2S,4S,6S)-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°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. $[\alpha]_{\text{D}}^{25} +6.47^{\circ}$ ($c=0.34$, CHCl_3). IR (CHCl_3): 3480 cm^{-1} . ¹H-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^+).

(2S,4S,6S)-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. $[\alpha]_{\text{D}}^{23} +2.84^{\circ}$ ($c=0.9$, CHCl_3). IR (film): 1587, 1425, 1365, 1243, 1160, 1112, 968, 822, 720, 690 cm^{-1} . ¹H-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^+).

(2S,4S,6S)-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°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. $[\alpha]_{\text{D}}^{24} -1.93^{\circ}$ ($c=1.0$, CHCl_3). IR (CHCl_3): 1422, 1200, 1108, 962, 818, 698 cm^{-1} . ¹H-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 $\text{C}_{30}\text{H}_{42}\text{O}_4\text{Si}$: 494.2769. Found: 494.2859.

(3S,5R,7R)-7-Acetoxy-1-(O-tert-butylidiphenylsilyl)-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. $[\alpha]_D^{23} - 3.31^\circ$ ($c = 1.55$, CHCl_3). IR (CHCl_3): 1725, 1425, 1370, 1254, 1108, 965, 695 cm^{-1} . $^1\text{H-NMR}$ (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 $\text{C}_{32}\text{H}_{46}\text{O}_5\text{Si}$: 538.3095. Found: 538.3103.

(3R,5R,7R)-7-Acetoxy-3,5-(O-cyclohexylidene)-3,5-dihydroxyoctanoic acid (10) A solution of **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. $[\alpha]_D^{23} + 4.26^\circ$ ($c = 0.95$, CHCl_3). IR (CHCl_3): 3300–2700, 1715, 1372, 1250, 960 cm^{-1} . $^1\text{H-NMR}$ (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 $\text{C}_{16}\text{H}_{26}\text{O}_6$: 314.1693. Found: 314.1710.

Methyl (3R,5R,7R)-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. $[\alpha]_D^{22} - 29.32^\circ$ ($c = 1.0$, CHCl_3). IR (CHCl_3): 3475, 1720, 1434, 1142, 840 cm^{-1} . $^1\text{H-NMR}$ (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^+).

(3R,5R,7R)-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. $[\alpha]_D^{21} + 19.9^\circ$ ($c = 0.48$, CHCl_3). IR (CHCl_3): 3400, 1725, 1268, 1078 cm^{-1} . $^1\text{H-NMR}$ (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 ($\text{M} + \text{NH}_4^+$).

Tarchoanthuslactone (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. $[\alpha]_D^{21} - 0.44^\circ$ ($c = 1.0$, CHCl_3). IR (CHCl_3): 1725, 1305, 1250, 900, 835 cm^{-1} . $^1\text{H-NMR}$ (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. $[\alpha]_D^{20} - 47.86^\circ$ ($c = 0.5$, CHCl_3). IR (CHCl_3): 1723, 1505, 1255, 900, 840 cm^{-1} . $^1\text{H-NMR}$ (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 ($\text{M} + \text{NH}_4^+$).

(iii) **Tarchoanthuslactone (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 tarchoanthuslactone (**1**) (3.3 mg, 98% yield) as a colorless oil. $[\alpha]_D^{23} - 74.6^\circ$ ($c = 0.4$, CHCl_3). IR (CHCl_3): 3600–3200, 1720, 1600, 1520, 1445, 1380, 1260, 1040 cm^{-1} . $^1\text{H-NMR}$ (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 $\text{C}_{17}\text{H}_{20}\text{O}_6$: 320.1234. Found: 320.1246.

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