Supporting Information

A Convergent Stereocontrolled Total Synthesis of (−)-Terpestacin

Yehua Jin and Fayang G. Qiu*

Laboratory of Molecular Engineering, and Laboratory of Natural Product Synthesis,
Guangzhou Institute of Biomedicine and Health, The Chinese Academy of Sciences,
190 Kaiyuan Boulevard, The Science Park of Guangzhou, 510530, Guangdong, China

qiu_fayang@gibh.ac.cn

General experimental details

$^1$H and $^{13}$C NMR spectra were recorded on either at 400 MHz ($^1$H) and 100 MHz ($^{13}$C) or at 500 MHz ($^1$H) and 125 MHz ($^{13}$C), and were internally referenced to residual proton solvent signals (note: CDCl$_3$ referenced at $\delta$7.26 and 77.0 ppm, respectively).

Data for $^1$H NMR were reported as follows: chemical shift ($\delta$ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant (Hz) and assignment. Data for $^{13}$C NMR were reported in terms of chemical shifts and no special nomenclature was used for equivalent carbons. High-resolution mass spectra (HRMS) were obtained using electrospray ionization (ESI) or electron ionization (EI). Optical Rotations were measured at 589 nm.

**Compound 6:** LiAlH$_4$ (4.9 g, 0.129 mol, 1 eq) was added over 20 min at RT to a stirred solution of 5 (36.39 g, 0.129 mol) in THF (360 mL). The reaction mixture was kept at RT for 3 h before it was quenched with H$_2$O (4.9 mL), followed by sequential addition of NaOH (2 M, 10 mL) and H$_2$O (15 mL). The resulting mixture was filtered on a Büchner funnel, and the solid was washed with ethyl acetate (5×60 mL). The combined organic extracts were concentrated under vacuum to give a crude oil (31.4 g) which was dissolved in CH$_2$Cl$_2$ (300 mL). Et$_3$N (20.6 mL) and BzCl (14.52 mL) were sequentially added to the reaction mixture at RT. The reaction mixture was kept at RT for 10 h before it was quenched with saturated NaHCO$_3$ (30 mL). The mixture was washed with water (100 mL). The organic layer was separated and the aqeous layer was back extracted with CH$_2$Cl$_2$ (3 × 50 mL). The combined organic extracts were
dried over MgSO₄, filtered and evaporated under reduced pressure to afford compound 6, which was purified via silica gel flash column chromatography to give a pale yellow oil (42.5 g, 92%, over two steps). Rf: 0.2 (petroleum ether/ethyl acetate = 30/1).

1H NMR (CDCl₃, 400 MHz): δ 8.02 (m, 4H), 7.55 (m, 2H), 7.43 (m, 4H), 4.83 (m, 2H), 4.73 (s, 2H), 4.71 (t, J = 3.4 Hz, 1H), 4.60 (dd, J = 4.6, 3.0 Hz, 1H), 4.26-4.20 (m, 3H), 4.12-4.04 (m, 3H), 3.92-3.86 (m, 2H), 3.53-3.48 (m, 2H), 3.08 (ddd, J = 9.5, 9.5, 8.1 Hz, 1H), 2.99 (ddd, J = 10.3, 10.3, 6.7 Hz, 1H), 2.28 (m, 2H), 2.09 (m, 2H), 2.02-1.66 (m, 8H), 1.80 (s, 6H), 1.62-1.45 (m, 8H), 1.21 (d, J = 7.0 Hz, 3H), 1.09 (d, J = 7.0 Hz, 3H).

13C NMR (CDCl₃, 125 MHz): δ 166.7, 144.75, 144.71, 132.8, 130.5, 129.5, 128.3, 111.04, 110.95, 100.4, 94.9, 81.0, 76.3, 66.6, 66.5, 62.8, 61.8, 45.1, 44.98, 44.96, 44.9, 42.6, 42.5, 37.6, 34.8, 31.1, 30.8, 25.6, 25.5, 23.70, 23.66, 19.9, 19.3, 14.8, 14.7.


**Compound 7 and compound 8:** To a solution of 6 (18.6 g, 0.052 mol, 1 eq) in THF (100 mL) at 0 °C was added BH₃-DMS (2 M in THF, 26 mL, 1 eq). After the reaction mixture was kept at 0 °C for 3 h, water (45 mL) was slowly added followed by the addition of sodium perborate (24 g, 3 eq). The mixture was maintained at room temperature (water bath) for 2 h with vigorous stirring. The two phases were separated, and the aqueous phase was extracted with ether (3 × 50 mL). The combined organic phase was washed with saturated NaCl solution (50 mL), dried over MgSO₄, filtered and evaporated under reduced pressure. The crude residue was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to provide compound 7 (10.2 g, 53%, Rf: 0.25: petroleum ether/ethyl acetate = 3/1) and compound 8 (6.8 g, 35%, Rf: 0.2: petroleum ether/ethyl acetate = 3/1). Both are pale yellow oil.

**Compound 7: **1H NMR (CDCl₃, 400 MHz): δ 8.03 (m, 4H), 7.56 (m, 2H), 7.45 (m, 4H), 4.68 (t, J = 3.4 Hz, 1H), 4.56 (dd, J = 4.6, 2.8 Hz, 1H), 4.46 (dd, J = 5.6, 5.6 Hz, 1H), 4.43 (dd, J = 5.5, 5.5 Hz, 1H, 4.24-4.14 (m, 4H), 3.89 (m, 2H), 3.71 (m, 2H), 3.50 (m, 2H), 3.42 (m, 2H), 2.37-2.11 (m, 6H), 1.99 (ddd, J = 13.4, 7.3, 1.9 Hz, 1H), 1.89-1.48 (m, 17H), 1.16 (d, J = 6.8 Hz, 3H), 1.05 (d, J = 6.8 Hz, 3H), 0.97 (d, J = 4.8 Hz, 3H), 0.96 (d, J = 4.8 Hz, 3H).

13C NMR (CDCl₃, 125 MHz): δ 166.8, 132.9, 130.3, 129.5, 128.4, 100.1, 95.4, 79.8, 75.8, 67.8, 67.7, 66.0, 65.9, 62.9, 62.0, 45.4, 45.3, 42.3, 42.1, 40.1, 39.9, 36.7, 35.8, 35.6, 34.2, 31.2, 30.8, 25.6, 25.5, 20.0, 19.4, 16.1, 16.0, 14.9, 14.8.
HRMS (ESI-TOF): calc’d for C_{22}H_{32}O_{3}Na [M + Na]^+: 399.2147, found: 399.2150.  
[α]_D^{20}: -18.0 (C = 1.65, CH_2Cl_2).

Compound 8: $^1$H NMR (CDCl$_3$, 400 MHz): δ 8.03 (m, 4H), 7.56 (m, 2H), 7.45 (m, 4H), 4.66 (t, J = 3.3 Hz, 1H), 4.54 (dd, J = 5.1, 2.6 Hz, 1H), 4.45 (dd, J = 6.7, 4.6 Hz, 1H), 4.43 (dd, J = 6.6, 4.5 Hz, 1H), 4.26 (m, 1H), 4.21-4.11 (m, 3H), 3.89 (m, 2H), 3.65 (m, 2H), 3.52-3.42 (m, 4H), 2.33-2.12 (m, 6H), 2.01 (dd, J = 13.0, 6.8, 1.5 Hz, 1H), 1.91-1.49 (m, 17H), 1.16 (d, J = 7.1 Hz, 3H), 1.10 (d, J = 6.5 Hz, 3H), 1.09 (d, J = 6.5 Hz, 3H), 1.06 (d, J = 7.1 Hz, 3H).

$^{13}$C NMR (CDCl$_3$, 125 MHz): δ 166.8, 132.9, 130.3, 129.5, 128.4, 100.0, 95.7, 80.0, 76.1, 67.5, 67.4, 65.9, 65.8, 63.2, 62.1, 45.33, 45.30, 41.5, 41.33, 41.27, 37.0, 35.8, 35.7, 34.8, 31.2, 30.9, 25.6, 25.5, 20.1, 19.5, 16.9, 16.8, 15.05, 15.01.

HRMS (ESI-TOF): calc’d for C_{22}H_{32}O_{3}Na [M + Na]^+: 399.2147, found: 399.2145.  
[α]_D^{20}: -18.6 (C = 1.23, CH_2Cl_2).

![Chemical Reaction Diagram](image)

**Compound 9:** To a solution of 7 (10.2 g, 0.027 mol, 1 eq) in CH$_2$Cl$_2$ (100 mL) was sequentially added diisopropylethylamine (5.20 mL, 1.1 eq) and MEMCl (3.13 mL, 1.01 eq) at RT. The reaction mixture was kept at RT for 3 h before it was quenched with saturated NaHCO$_3$ (30 mL). The mixture was washed with water (50 mL). The organic layer was separated and the aqueous layer was back extracted with CH$_2$Cl$_2$ (3 × 40 mL). The combined organic extracts were dried over MgSO$_4$, filtered on silica gel, and evaporated under reduced pressure to afford crude compound 7a (11.6 g, 92%) as a yellow oil, which was used without further purification.

To a solution of 7a in MeOH (100 mL) was added NaOH (0.9962 g). After 10 h, the reaction mixture was concentrated to about 50 mL, diluted with ether (150 mL) and washed with water (100 mL). The organic layer was separated and the aqueous layer was back extracted with ether (3 × 50 mL). The combined organic extracts were dried over MgSO$_4$, filtered and evaporated under reduced pressure to afford compound 7b, which was purified via silica gel flash column chromatography (petroleum ether/ethyl acetate = 2/1) to give a pale yellow oil (7b, 8.1 g, 90%, R$_f$: 0.25: petroleum ether/ethyl acetate = 2/1).
To a solution of 7b (8.1 g, 0.0225 mol) in CH2Cl2 (100 mL) was added TEMPO (0.1756 g, 0.05 eq) and diacetoxyiodobenzene (7.9 g, 1.1 eq) at RT. The reaction mixture was kept at RT for 3 h before it was quenched with saturated NaHCO3 (20 mL). The mixture was washed with water (50 mL). The aqueous layer was back extracted with CH2Cl2 (3 × 40 mL). The combined organic extracts were dried over MgSO4, filtered, and evaporated under reduced pressure to afford compound 7c, which was purified via silica gel flash column chromatography (petroleum ether/ethyl acetate = 3/1) to give a pale yellow oil (7c, 7.9 g, 98%, Rf: 0.33: petroleum ether/ethyl acetate = 3/1).

In a flame dried, argon purged round bottom flask, methyltriphenylphosphonium bromide (7.9 g, 1 eq) and THF (60 mL) was added. The flask was cooled to −20 °C, and then NaHMDS (1 M in THF, 22.1 mL, 1 eq) was added dropwise. The reaction mixture was kept at −20 °C for 2 h before 7c (7.9 g, 0.0221 mol, 1 eq) in THF (20 mL) was added dropwise. The reaction mixture was kept at −20 °C for 1 h, warmed to 0 °C and stirred for 1 h. The reaction solution was poured into a mixture of ether (300 mL) and water (200 mL). The two phases were separated, and the aqueous layer was back extracted with ether (3 × 50 mL). The combined organic extracts were dried over MgSO4, filtered and evaporated under reduced pressure to afford compound 9, which was purified via silica gel flash column chromatography (petroleum ether/ethyl acetate = 10/1) to give a pale yellow oil (9, 7.1 g, 91%, Rf: 0.25: petroleum ether/ethyl acetate = 10/1).

Compound 9: 1H NMR (CDCl3, 400 MHz): δ 5.73 (m, 2H), 4.99 (m, 4H), 4.69-4.66 (5H, including Single at 4.68), 4.55 (dd, J = 4.6, 2.8 Hz, 1H), 4.14 (ddd, J = 4.8, 4.8, 1.0 Hz, 1H), 4.10 (ddd, J = 5.6, 5.6, 2.0 Hz, 1H), 3.88 (m, 2H), 3.66 (m, 4H), 3.59-3.54 (m, 6H), 3.49 (m, 2H), 3.39 (s, 6H), 3.20 (dd, J = 7.7, 1.9 Hz, 1H), 3.17 (dd, J = 7.8, 1.8 Hz, 1H), 2.32 (m, 2H), 2.18 (m, 2H), 1.94 (ddd, J = 13.4, 7.6, 2.1 Hz, 1H), 1.88-1.39 (m, 19H), 1.03 (d, J = 7.0Hz, 3H), 0.924 (d, J = 7.4Hz, 3H), 0.918 (d, J = 6.6 Hz, 3H), 0.91 (d, J = 6.9 Hz, 3H).

13C NMR (CDCl3, 125 MHz): δ 139.9, 139.7, 115.13, 115.05, 99.8, 95.6, 95.2, 80.3, 76.5, 72.2, 72.1, 71.8, 66.6, 66.5, 62.8, 61.8, 59.0, 52.3, 52.1, 45.3, 45.1, 41.3, 41.1, 36.4, 34.2, 34.0, 33.8, 31.2, 30.8, 25.65, 25.55, 19.9, 19.3, 16.2, 16.1, 13.5, 13.3.


**Compound 10:** To a solution of 9 (7.0 g, 0.0196 mol, 1 eq) in THF (100 mL) at 0 °C was added BH3•THF (1 M in THF, 23.6 mL, 1.2 eq). After the reaction mixture was kept at 0 °C for 5 h, NaOH (3 M, 23.6 mL, 3.6 eq) was slowly added followed by the
addition of H$_2$O$_2$ (34% in water, 8 mL, 3.6 eq) and the mixture was maintained at the same temperature for 2 h with vigorous stirring. The mixture was diluted with ether (200 mL), washed with water (100 mL) and saturated NH$_4$Cl (100 mL). The aqueous layer was back extracted with ether (3 × 80 mL). The combined organic phase was washed with saturated NaCl solution (100 mL) and dried over MgSO$_4$, filtered and evaporated under reduced pressure to afford compound 10, which was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 2/1) to give a pale yellow oil (10, 6.5 g, 88%, Rf: 0.25; petroleum ether/ethyl acetate = 3/2).

$^1$H NMR (CDCl$_3$, 400 MHz): δ 4.69 (m, 4H), 4.62 (t, J = 3.3 Hz, 1H), 4.50 (m, 1H), 4.17 (m, 2H), 3.87 (m, 2H), 3.73-3.54 (m, 14H), 3.47 (m, 2H), 3.34 (s, 6H), 3.18 (d, J = 8.7 Hz, 1H), 3.16 (d, J = 8.6 Hz, 1H), 2.14-1.43 (m, 28H, including –OH), 1.28 (m, 2H), 1.03 (d, J = 7.1 Hz, 3H), 0.94 (d, J = 6.5 Hz, 3H), 0.92 (d, J = 6.8 Hz, 6H).

$^{13}$C NMR (CDCl$_3$, 125 MHz): δ 99.3, 96.0, 95.36, 95.34, 78.8, 75.9, 72.0, 71.9, 66.74, 66.73, 62.8, 62.1, 61.7, 61.6, 59.0, 43.4, 43.0, 42.8, 42.3, 40.9, 40.8, 35.7, 33.7, 33.5, 32.8, 32.4, 31.2, 30.8, 25.6, 25.5, 19.9, 19.5, 16.7, 16.5, 15.07, 15.05. HRMS (ESI-TOF): calc’d for C$_{20}$H$_{32}$O$_6$Na [M + Na]$^+$: 397.2566, found: 397.2562. [$\alpha$]$_D^{20}$: −14.7 (C = 3.38, CH$_2$Cl$_2$).

**Compound 11**: To a solution of 10 (6.3 g, 0.0168 mol, 1 eq) in CH$_2$Cl$_2$ (100 mL) at RT was added Et$_3$N (3 mL, 1.3 eq), TBSCI (2.78 g, 1.1 eq) and DMAP (0.1 g, 0.05 eq). After being kept at RT for 8 h, the reaction mixture was washed with water (50 mL). The aqueous layer was back extracted with CH$_2$Cl$_2$ (3 × 50 mL). The combined organic phase was washed with saturated NaCl solution (50 mL) and dried over MgSO$_4$, filtered and evaporated under reduced pressure to afford compound 11, which was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to give a pale yellow oil (11, 8.1 g, 98%, Rf: 0.5; petroleum ether/ethyl acetate = 5/1).

$^1$H NMR (CDCl$_3$, 400 MHz): δ 4.69 (s, 4H), 4.62 (t, J = 3.3 Hz, 1H), 4.51 (dd, J = 4.6, 2.5 Hz, 1H), 4.17 (m, 2H), 3.88 (m, 2H), 3.72-3.54 (m, 12H), 3.48 (m, 4H), 3.39 (s, 6H), 3.24 (d, J = 6.8 Hz, 1H), 3.21 (d, J = 8.2 Hz, 1H), 2.15-1.45 (m, 26H), 1.23 (m, 2H), 1.02 (d, J = 7.1 Hz, 3H), 0.93 (d, J = 6.1 Hz, 3H), 0.92 (d, J = 6.2 Hz, 3H), 0.91 (d, J = 7.2 Hz, 3H), 0.89 (s, 18H), 0.042 (s, 6H), 0.041 (s, 6H).

$^{13}$C NMR (CDCl$_3$, 125 MHz): δ 99.3, 96.0, 95.7, 78.8, 76.0, 72.3, 72.2, 71.8, 66.7, 66.6, 62.8, 62.13, 62.06, 59.0, 43.17, 43.14, 42.9, 42.0, 40.8, 40.6, 35.6, 33.7, 33.5, 32.4, 32.0, 31.2, 30.8, 26.0, 25.64, 25.55, 19.9, 19.5, 18.3, 16.5, 16.3, 15.01, 14.97, −5.3.

HRMS (ESI-TOF): calc’d for C$_{26}$H$_{52}$O$_6$SiNa [M + Na]$^+$: 511.3431, found: 511.3424.
\[ \alpha \]_D^{20} = -2.89 (C = 2.04, CH_2Cl_2).

**Compound 12:** To a solution of 11 (8.0 g, 0.0164 mol, 1 eq) in ether (100 mL) at RT was added the solution of MgBr_2 (5 eq) in ether (100 mL) (prepared from the reaction of Mg and 1,2-dibromoethane). The reaction mixture was kept at RT for 16 h before it was quenched with saturated NaHCO_3 (100 mL). The mixture was washed with water (100 mL). The aqueous layer was back extracted with ether (3 × 80 mL). The combined organic phase was dried over MgSO_4, filtered and evaporated under reduced pressure to afford compound 12, which was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 4/1) to give a pale yellow oil (12, 6.2 g, 94% , R_f: 0.3: petroleum ether/ethyl acetate = 3/1).

1H NMR (CDCl_3, 400 MHz): δ 4.69 (s, 2H), 4.18 (m, 1H), 3.69 - 3.54 (m, 6H), 3.47 (dd, J = 9.4, 4.6 Hz, 1H), 3.39 (s, 3H), 3.24 (dd, J = 9.3, 7.6 Hz, 1H), 2.18 (m, 1H), 1.87 (m, 1H), 1.80 (m, 1H), 1.75-1.64 (m, 4H), 1.30 (br, 1H), 1.26 (m, 1H), 0.99 (d, J = 6.6 Hz, 3H), 0.92 (d, J = 6.6 Hz, 3H), 0.89 (s, 9H), 0.04 (s, 6H).

13C NMR (CDCl_3, 125 MHz): δ 95.6, 74.0, 72.4, 71.8, 66.7, 62.1, 59.0, 44.2, 42.7, 40.6, 37.3, 33.2, 32.7, 25.9, 18.3, 16.1, 14.4, −5.3.

HRMS (ESI-TOF): calc’d for C_{21}H_{44}O_5SiNa [M + Na]^+: 427.2856, found: 427.2874.

[\alpha]_D^{20} = +8.0 (C = 1.63, CH_2Cl_2).

**Compound 3:** To a solution of 12 (6.0 g, 0.0148 mol) in CH_2Cl_2 (100 mL) was added TEMPO (0.116 g, 0.05 eq) and diacetoxyiodobenzene (5.3 g, 1.1 eq) at RT. The reaction mixture was kept at RT for 3 h, before quenched with saturated NaHCO_3 (20 mL). The mixture was wash with water (50 mL). The aqueous layer was back extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were dried over MgSO_4, filtered and evaporated under reduced pressure to afford compound 3, which was purified via silica gel flash column chromatography (petroleum ether/ethyl acetate = 7/1) to give a pale yellow oil (3, 5.7 g, 96%, R_f: 0.2: petroleum ether/ethyl acetate = 7/1).

1H NMR (CDCl_3, 400 MHz): δ 4.71 (s, 2H), 3.72-3.55 (m, 6H), 3.50 (dd, J = 9.4, 4.8 Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Hz, 1H), 3.39 (s, 3H), 3.37 (dd, J = 9.5, 6.8 Hz 1H), 2.36-2.26 (m, 2H), 2.17 (m, 1H), 2.12-2.02 (m, 2H), 1.95 (m, 1H), 1.78 (m, 1H), 1.36 (m, 1H), 1.09 (d, J = 7.5 Hz, 3H), 0.93 (d, J = 6.7 Hz, 3H), 0.89 (s, 9H), 0.04 (s, 6H).

$^{13}$C NMR (CDCl$_3$, 125 MHz): δ 221.8, 95.7, 71.8, 71.1, 66.8, 61.2, 59.0, 48.6, 42.0, 40.2, 38.6, 33.4, 31.3, 25.9, 18.3, 16.1, 15.9, −5.37, −5.40.


$[\alpha]_{D}^{20}$: −24.6 (C = 1.95, CH$_2$Cl$_2$).

**Compound (13a, 13b):** To a solution of 3 (0.750 g, 0.00186 mol, 1 eq) in THF (7 mL) at RT was slowly added NaHMDS (2 M in THF, 0.88 mL, 0.95 eq) during 1h, the solution was stirred at RT for additional hour. Allylic bromide 4 (1.00 g, 1 eq) in THF (7 mL) was added. The reaction mixture was kept at RT for 30 min. The reaction mixture was diluted with ether (50 mL) and then quenched with saturated NH$_4$Cl (7 mL) and water (20 mL). The organic layer was separated and the aqueous layer was back extracted with ether (3 × 30 mL). The combined organic phase was washed with saturated NaCl solution (50 mL), dried over MgSO$_4$, filtered and evaporated under reduced pressure. The crude residue was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 2/1) to give a mixture of isomers as a pale yellow oil (13a and 13b, 1.48g, 93%, Rf: 0.25: petroleum ether/ethyl acetate = 2/1) (13a/13b = 3:1).
Compound 14: To a solution of the mixture of 13a and 13b (13a:13b = 3:1) (1.40 g) in THF (20 mL) was added nBu4NF (1 M in THF, 3.42 mL, 2.1 eq). The reaction mixture was kept at RT for 7 h, before it was quenched with saturated NH4Cl (20 mL). The mixture was diluted with ether (50 mL) and water (30 mL) was added. The organic layer was separated and the aqueous layer was extracted with ether (3 × 30 mL). The combined organic phase was dried over MgSO4, filtered and evaporated under reduced pressure. The crude residue was purified by using flash chromatography on silica gel (CH2Cl2/MeOH = 30:1) to give a pale yellow oil mixture of diol isomers (0.96 g, 93%, Rf: 0.2; CH2Cl2/MeOH = 30:1).

To the above diol isomers (0.96 g, 1.52 mmol) in DMSO (5 mL) was added IBX (0.93 g, 2.2 eq). The reaction mixture was kept at RT for 5 h. The reaction mixture was diluted with ether (50 mL) and water (50 mL) was added. The organic layer was separated and the aqueous layer was back extracted with ether (3 × 50 mL). The combined organic phase was washed with saturated NaCl solution (30 mL), dried over MgSO4, filtered and evaporated under reduced pressure. The crude residue was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 1/5) to give a pale yellow oil mixture of ketoaldehyde isomers (0.76 g, 80%, Rf: 0.33: petroleum ether/ethyl acetate = 1/5).

To the above ketoaldehyde isomers (0.76 g, 1.21 mmol) in CH3CN (240 mL) was added LiCl (0.51 g, 10 eq) and DIPEA (2.1 mL, 10 eq). The reaction mixture was kept at RT for 6 days. The mixture was concentrated under reduced pressure, dissolved in CH2Cl2 (50 mL) and water (50 mL) was added. The organic layer was separated and the aqueous layer was extracted with ether (3 × 30 mL). The combined organic phase was dried over MgSO4, filtered and evaporated under reduced pressure to afford compound 14, which was purified by using flash chromatography on silica gel.
gel (petroleum ether/ethyl acetate = 4/1) to give a pale yellow oil (14, 0.373 g, 65%, Rf: 0.2: petroleum ether/ethyl acetate = 4/1).

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 6.50 (t, 4.8 Hz, 1H), 5.13 (m, 2H), 4.71 (s, 2H), 3.67 (dd, J = 5.7, 3.6 Hz, 2H), 3.57 (dd, J = 9.5, 4.1, Hz, 1H), 3.53 (dd, J = 5.7, 3.5 Hz, 2H), 3.40 (dd, J = 9.5, 6.6 Hz, 1H), 3.37 (s, 3H), 2.77 (ddd, J = 14.7, 9.3, 5.5 Hz, 1H), 2.56 (m, 1H), 2.52-2.41 (m, 3H), 2.30-1.89 (m, 12H), 1.71 (s, 3H), 1.62 (s, 6H), 1.06 (d, J = 6.6 Hz, 3H), 0.95 (s, 3H).

\(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \(\delta\) 221.7, 202.4, 144.8, 138.5, 135.7, 134.9, 123.3, 120.1, 95.8, 71.7, 71.2, 66.9, 59.1, 56.1, 44.0, 40.5, 40.2, 39.7, 36.8, 36.5, 34.4, 24.9, 23.8, 17.9, 17.3, 16.0, 15.7, 11.4.

HRMS (ESI-TOF): calc’d for C\(_{29}\)H\(_{46}\)O\(_5\)Na \([M + Na]^+\): 497.3243, found: 497.3242.

[\(\alpha\)]\(_D\)\(^{20}\): +1.9 (C = 0.94, CH\(_2\)Cl\(_2\)).

### Compound 14a:
A solution of 14 (0.136 g, 0.29 mmol) in THF (4 mL) was cooled to \(-50^\circ C\). To this solution was slowly added BH\(_3\) (1.7 eq, 1 M in THF), then slowly added R-(Me)-CBS (1 eq, 1 M in toluene) in 1 h. The reaction mixture was kept at this temperature for 1 h and then quenched with MeOH (1 mL) then saturated NH\(_4\)Cl (3 mL). The mixture was allowed to warm to RT, diluted with ether (10 mL), washed with water (10 mL). The aqueous layer was back extracted with ether (3 \(\times\) 10 mL). The combined organic phase was washed with saturated NaCl solution (10 mL), dried over MgSO\(_4\), filtered and evaporated under reduced pressure to afford compound 14a, which was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 2/1) to give the starting material (14, 0.045 g) and a colorless oil [14a, 0.068 g, 50% (75% BORSM), Rf: 0.25: petroleum ether/ethyl acetate = 2/1).

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 5.17 (m, 3H), 4.71 (s, 2H), 3.94 (m, 1H), 3.68 (d, J = 5.5 Hz, 1H), 3.67 (d, J = 5.7 Hz, 1H), 3.61 (d, J = 9.4, 3.5 Hz, 1H), 3.56 (d, J = 5.7 Hz, 1H), 3.55 (d, J = 5.3 Hz, 1H), 3.39 (s, 3H), 3.30 (dd, J = 9.2, 7.2 Hz, 1H), 2.40 (dd, J = 17.4, 5.5 Hz, 1H), 2.26-1.79 (m, 14H), 1.68-1.62 (m, 2H), 1.62 (s, 6H), 1.56 (s, 3H), 1.05 (d, J = 6.5 Hz, 3H), 1.01 (s, 3H).

\(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 222.9, 137.5, 135.3, 133.1, 130.6, 124.4, 121.7, 95.6, 76.8, 71.7, 70.7, 66.6, 58.9, 55.6, 44.5, 41.1, 40.1, 39.7, 35.1, 34.9, 34.7, 29.8, 23.8, 22.8, 17.8, 17.3, 15.9, 15.4, 10.8.

HRMS (EI-TOF): calc’d for C\(_{29}\)H\(_{48}\)O\(_5\) \([M]^+\): 476.3502, found: 476.3510.
1. PPTS, t-BuOH, reflux

2. TBSCl, Et3N, DMAP

CH2Cl2, RT

(2 steps 70%)

Compound 15: To a solution of 14 (0.35 g, 0.74 mmol) in t-BuOH (5 mL) was added PPTS (2 eq). The reaction mixture was refluxed for 8 h, diluted with ether (30 mL) and water (30 mL) was added. The organic layer was separated and the aqueous layer was extracted with ether (3 x 50 mL). The combined organic phase was washed with saturated NaCl solution (30 mL), dried over MgSO4, filtered and evaporated under reduced pressure. The crude residue was dissolved in CH2Cl2 (10 mL) and added TBSCl (1.5 eq), DMAP (0.05 eq) and Et3N (2 eq). The reaction mixture was kept at RT for 10 h. The mixture was wash with water (30 mL). The aqueous layer was back extracted with CH2Cl2 (3 x 30 mL). The combined organic phase was washed with saturated NaCl solution (30 mL), dried over MgSO4, filtered and evaporated under reduced pressure to afford compound 15, which was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to give a colorless oil (15, 0.258 g, 70%, Rf: 0.2; petroleum ether/ethyl acetate = 10/1).

1H NMR (CDCl3, 400 MHz): δ 6.51 (t, J = 5.3 Hz, 1H), 5.15 (m, 2H), 3.60 (dd, J = 9.9, 4.0 Hz, 1H), 3.50 (dd, J = 9.9, 5.6 Hz, 1H), 2.76 (dd, J = 14.8, 9.3, 5.5 Hz, 1H), 2.57 (m, 1H), 2.48-2.42 (m, 3H), 2.38 -1.90 (m, 11H), 1.81 (m, 1H), 1.71 (s, 3H), 1.63 (s, 3H), 1.62 (s, 3H), 1.00 (d, J = 6.6 Hz, 3H), 0.94 (s, 3H), 0.90 (s, 9H), 0.05 (s, 6H).

13C NMR (CDCl3, 125 MHz): δ 220.0, 202.4, 145.0, 138.4, 135.7, 134.9, 123.3, 120.2, 66.3, 56.1, 44.0, 40.5, 40.2, 39.2, 36.8, 36.5, 36.4, 34.4, 25.9, 25.0, 23.9, 18.4, 18.0, 16.9, 16.0, 15.7, 11.4, −5.4.


[α]D20: +18.9 (C = 0.95, CH2Cl2).

Compound 16: A solution of 15 (0.32 g, 0.64 mmol) in THF (8 mL) was cooled to −50 °C. To this solution was slowly added BH3 (1.7 eq, 1 M in THF), then slowly added R-(Me)-CBS (1 eq, 1 M in toluene) in 1 h. The reaction mixture was kept at
this temperature for 1 h and then quenched with MeOH (2 mL) then saturated NH₄Cl (7 mL). The mixture was allowed to warm to RT, diluted with ether (20 mL), washed with water (20 mL). The aqueous layer was back extracted with ether (3 × 30 mL). The combined organic phase was washed with saturated NaCl solution (10 mL), dried over MgSO₄, filtered and evaporated under reduced pressure to afford compound 16, which was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 to 5/1) to give the starting material (15, 0.106 g) and a colorless oil [16, 0.161 g, 50% (75% BORSM), Rf: 0.25; petroleum ether/ethyl acetate = 6/1).

**1H NMR (CDCl₃, 400 MHz):** δ 5.17 (m, 3H), 3.97 (dd, J = 9.1, 3.7 Hz, 1H), 3.60 (dd, J = 9.8, 3.6 Hz, 1H), 3.43 (dd, J = 9.8, 6.1 Hz, 1H), 2.36 (ddd, J = 17.4, 6.5, 1.3 Hz, 1H), 2.27-1.66 (m, 16 H), 1.64 (s, 3H), 1.63 (s, 3H), 1.57 (s, 3H), 0.99 (d, J = 6.2 Hz, 3H), 1.00 (s, 3H), 0.89 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H).

**13C NMR (CDCl₃, 125 MHz):** δ 223.1, 137.4, 135.2, 133.3, 130.4, 124.3, 121.7, 76.95, 65.8, 55.5, 44.4, 41.0, 39.7, 39.4, 36.5, 34.9, 30.1, 25.9, 23.8, 23.0, 18.4, 17.9, 16.8, 15.9, 15.5, 11.1, −5.37, −5.39.

**HRMS (ESI-TOF):** calc’d for C₃₁H₅₅O₃Si [M + H]+: 503.3920, found: 503.3919.

**Compound 17:** A solution of 16 (0.15 g, 0.30 mmol) and 2.6 lutidine (0.07 mL, 2 eq) in CH₂Cl₂ (8 mL) was cooled to −78 °C. To this solution was slowly added TBSOTf (0.07 mL, 1.05 eq). The reaction mixture was kept at this temperature for 1 h, and then quenched with MeOH (1 mL). The mixture was allowed to warm to RT, washed with water (20 mL). The aqueous layer was back extracted with CH₂Cl₂ (3 × 20 mL). The combined organic phase was washed with saturated NaCl solution (10 mL), dried over MgSO₄, filtered and evaporated under reduced pressure to afford compound 17, which was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 30/1) to give a colorless oil (17, 0.178 g, 97%, Rf: 0.25; petroleum ether/ethyl acetate = 30/1).

**1H NMR (CDCl₃, 400 MHz):** δ 5.18 (t, 8.0 Hz, 1H), 5.13 (m, 1H), 5.00 (m, 1H) 3.92 (dd, J = 8.2, 5.3 Hz, 1H), 3.63 (dd, J = 9.8, 3.3 Hz, 1H), 3.40 (dd, J = 9.8, 6.7 Hz, 1H), 2.36 (dd, J = 17.1, 6.1 Hz, 1H), 2.26-1.66 (m, 16H), 1.63 (s, 3H), 1.61 (s, 3H), 1.50 (s, 3H), 1.00 (d, J = 6.6 Hz, 3H), 0.97 (s, 3H), 0.90 (s, 9H), 0.85 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H), 0.00 (s, 6H).

**13C NMR (CDCl₃, 125 MHz):** δ 223.3, 137.5, 136.3, 133.0, 128.7, 123.5, 121.8, 77.5, 65.7, 55.4, 44.5, 41.1, 39.9, 39.4, 36.5, 35.1, 34.7, 31.6, 25.94, 25.86, 23.8, 22.8, 18.4, 18.1, 18.0, 16.8, 15.9, 10.8, −4.6, −4.8, −5.3, −5.4.
HRMS (EI-TOF): calc’d for C$_{37}$H$_{68}$O$_3$Si$_2$ [M]$^+$: 616.4707, found: 616.4714
\[\alpha\]$_D^{20}$: −31.8 (C = 0.44, CH$_2$Cl$_2$).

**Compound 18:** A solution of 17 (0.16 g, 0.26 mmol) in THF (5 mL) was cooled to −45 °C. To this solution was slowly added NaHMDS (1.5 eq, 2 M in THF). The reaction mixture was kept at this temperature for 1 h, and then cooled to −78 °C. To this solution was slowly added N-Sulfonyloxaziridines (1.5 eq) in THF (1 mL). The reaction mixture was kept at −78 °C for 1 h, then quenched with saturated NH$_4$Cl (2 mL). The mixture was stirred at −78 °C for 1 h, and then allowed to warm to RT. The mixture was diluted with ether (20 mL) and washed with water (20 mL). The aqueous layer was back extracted with ether (3 × 30 mL). The combined organic phase was washed with saturated NaCl solution (10 mL), dried over MgSO$_4$, filtered and evaporated under reduced pressure. The crude residue was dissolved in MeOH (5 mL). To this solution was added Cu(OAc)$_2$ (50 eq). The reaction mixture was kept at RT for 10 h, and then diluted with ether (20 mL), washed with water (20 mL). The aqueous layer was back extracted with ether (3 × 30 mL). The combined organic phase was dried over MgSO$_4$, filtered and evaporated under reduced pressure to afford compound 18, which was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give a colorless oil (18, 0.129 g, 79%, Rf: 0.2: petroleum ether/ethyl acetate = 20/1).

$^1$H NMR (CDCl$_3$, 400 MHz): δ 6.45 (brs, 1H), 5.25 (m, 2H), 5.13 (m, 1H), 4.03 (dd, J = 8.2, 5.4 Hz, 1H), 3.84 (dd, J = 9.6, 6.5 Hz, 1H), 3.80 (dd, J = 9.6, 4.9 Hz, 1H), 2.66 (dd, J = 11.3, 2.3 Hz, 1H), 2.61 (m, 1H), 2.45-2.26 (m, 4H), 2.16-1.94 (m, 3H), 1.82 (m, 2H), 1.75-1.59 (m, 3H), 1.65 (s, 3H), 1.62 (s, 3H), 1.51 (s, 3H), 1.25 (dd, J = 7.1 Hz, 3H), 0.98 (s, 3H), 0.90 (s, 9H), 0.87 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H), 0.01 (s, 3H), −0.02 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 125 MHz) δ 207.8, 149.1, 146.8, 138.0, 137.3, 132.9, 126.7, 123.8, 121.7, 76.7, 66.8, 49.6, 48.9, 40.5, 39.0, 37.0, 34.5, 31.5, 28.3, 25.90, 25.89, 23.9, 18.3, 18.2, 16.5, 16.0, 15.4, 14.5 10.4, 4.6, −4.8, −5.46, −5.50.

HRMS (ESI-TOF): calc’d for C$_{37}$H$_{67}$O$_3$Si$_2$ [M + H]$^+$: 631.4578, found: 631.4575.

\[\alpha\]$_D^{20}$: +3.0 (C = 0.37, CH$_2$Cl$_2$).
(-)-Terpestacin 1a: To a solution of 18 (0.100 g 0.158 mmol) in THF (3 mL) was added aqueous HF (46%, 0.3 mL). The reaction mixture was kept at RT for 3 h. The mixture was diluted with ether (20 mL) and washed with water (20 mL). The aqueous layer was back extracted with ether (3 x 20 mL). The combined organic phase was washed with saturated NaHCO₃ (30 mL), dried over MgSO₄, filtered and evaporated under reduced pressure to afford (-)-terpestacin 1a, which was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 1/1) to give a white solid (1a, 0.057 g, 90%, Rf: 0.33: petroleum ether/ethyl acetate = 1/1).

¹H NMR (CDCl₃, 400 MHz): δ = 5.94 (brs, 1H), 5.39 (m, 1H), 5.23 (dd, J = 10.3, 5.2 Hz, 1H), 5.12 (m, 1H), 4.05 (dd, J = 9.8, 3.5 Hz, 1H), 3.88 (dd, J = 10.4, 7.0 Hz, 1H), 3.81 (dd, J = 10.4, 5.4 Hz, 1H), 2.70 (dd, J = 11.4, 2.1 Hz, 1H), 2.67 (m, 1H), 2.43 (dd, J = 17.2 Hz, 1H), 2.37 (dd, J = 13.7, 10.6 Hz, 1H), 2.29-2.23 (m, 2H), 2.12-2.07 (m, 2H), 2.04-1.88 (m, 2H), 1.81-1.65 (m, 4H), 1.63 (s, 3H), 1.62 (s, 3H), 1.56 (s, 3H), 1.29 (d, J = 7.1 Hz, 3H), 0.98 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz) δ 208.1, 149.3, 146.8, 138.0, 136.4, 132.9, 129.0, 124.3, 121.6, 76.5, 66.0, 49.6, 49.0, 40.3, 39.3, 37.1, 34.9, 29.8, 28.8, 23.8, 16.2, 15.5, 15.3, 14.3, 10.4.


[α]D²⁰: −27.5 (C = 1.54, CHCl₃); [α]D²⁰: −21.1 (C = 1.07, MeOH).
(-)-terpestatin from this work
(2mg) in CDCl$_3$ (0.5ml)
\(-\)-terpestacin from this work
(14 mg) in CDCl\textsubscript{3} (0.5 mL)

Natural terpestacin (Arthriniun)