Supplementary Material for Organic & Biomolecular Chemistry

The First Total Synthesis of Xenitorins B and C: Assignment of Absolute Configuration

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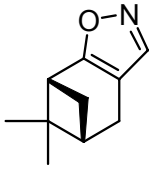
Experimental

(1*R*,8*R*)-9,9-Dimethyl-3-oxa-4-aza-tricyclo[6.1.1.$0^{2,6}$]deca-2(6),4-diene

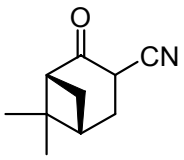


(-)-9

To a solution of compound **8** (2.01 g, 12.13 mmol) in ethanol (50 mL) at 0 °C was added potassium carbonate (2.55 g, 18.19 mmol) followed by hydroxylamine hydrochloride (1.70 g, 14.13 mmol). The reaction mixture thus obtained was refluxed for 2 h and then quenched with water followed by acidification with concentrated HCl solution. The aqueous layer was extracted with CH_2Cl_2 (3 x 30 mL) and the combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give the crude product which was chrmatographed over silica gel (*n*-hexane:ethyl acetate = 9:1) to afford compound **9** (1.57 g, 79%) as a light yellow oil.

IR (cast, $CHCl_3$, cm^{-1}): 1706, 1619 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 3.03 (t, *J* = 4 Hz, 1H), 2.73 (td, *J* = 3.8, 7.6 Hz, 1H), 2.61 (qd, *J* = 18.4, 2.4 Hz, 2H), 2.33~2.29 (m, 2H), 1.41 (s, 3H), 0.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.8 (C), 148.6 (CH), 106.5 (C), 41.9 (C), 41.8 (CH), 41.4 (CH), 32.0 (CH_2), 26.0 (CH_3), 23.0 (CH_2), 21.2 (CH_3); HRMS (EI): Cacld. for $C_{10}H_{13}NO$: 163.0996; found 163.0997; $[\alpha]_{20}^{D}$ = -29.1° (c = 5.7, $CHCl_3$).

(1*R*,5*R*)-6,6-Dimethyl-2-oxo-bicyclo[3.1.1]heptane-3-carbonitrile

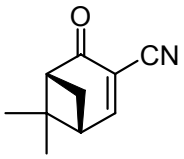


(+)-10

A solution of compound **9** (2.85 g, 17.5 mmol) in absolute EtOH (10 mL) was added dropwise into a stirred solution of freshly prepared NaOEt (35 mmol) in EtOH (20 mL) at 0 °C. The resulting reaction mixture was allowed to warm to rt and stirred at rt for 6 h. Excess base was then neutralized by the addition of aqueous 2N HCl and the aqueous layer was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product thus obtained was purified by flash chromatography over silica gel (*n*-hexane:ethyl acetate = 4:1) to give compound **10** (2.65 g, 93%) as a yellowish solid.

IR (cast, $CHCl_3$, cm^{-1}): 2246 (CN), 1725 (C=O) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.71 (dd, *J* = 8.0, 7.2 Hz, 1H), 2.71 (t, *J* = 4.8 Hz, 1H), 2.54~2.62 (m, 2H), 2.30 (q, *J* = 4.8 Hz, 1H), 2.16~2.22 (m, 1H), 1.59 (d, *J* = 11.2 Hz, 1H), 1.35 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.6 (C), 117.5 (C), 56.3 (CH), 42.6 (C), 39.2 (CH), 34.9 (CH), 27.0 (CH_2), 25.5 (CH_3), 23.8 (CH_2), 21.6(CH_3); HRMS (EI): Cacld. for $C_{10}H_{13}NO$: 163.0997; found 163.0997; $[\alpha]_{20}^{D}$ = +40.0° (c = 3.2, $CHCl_3$); mp 71-72 °C.

(1*R*,5*R*)-6,6-Dimethyl-4-oxo-bicyclo[3.1.1]hept-2-ene-3-carbonitrile



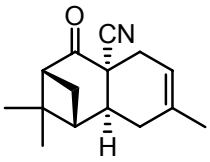
(+)-4

To a solution of phenylselenenyl chloride (1.05 g, 5.50 mmol) in CH_2Cl_2 (25 ml) at 0 °C was added pyridine (0.55 mL, 6.88 mmol). After stirring for 20 min, a solution of compound **10** (0.74 g, 4.58 mmol) in CH_2Cl_2 (5 mL) was introduced over a period of 10 min at 0 °C. The reaction mixture thus obtained was allowed to warm to rt and

stirred overnight. Excess pyridine was removed by sequential washing of the organic layer with 1N $HCl_{(aq)}$. The remaining organic layer was cooled to 0 °C and treated with H_2O_2 (30 %, 1.18 mL, 13.76 mmol) to effect the oxidative elimination process. Water was added and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, concentrated under reduced pressure, and the crude product thus obtained was subjected to flash chromatography on silica gel (ethyl acetate:*n*-hexane = 1:10) to furnish compound **4** (0.71 g, 97%) as a white solid.

IR (neat, cm^{-1}): 2231 (CN), 1704 (C=O) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.23 (dd, *J* = 5.6, 2.0 Hz,1H), 2.90~2.94 (m, 1H), 2.85 (t, *J* = 4.8 Hz, 1H), 2.80 (q, *J* = 4.8 Hz, 1H), 2.17 (d, *J* = 8.0 Hz, 1H), 1.53 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 195.5 (C), 169.1 (CH), 113.5 (C), 113.4 (C), 57.4 (CH), 55.2 (C), 44.5 (CH), 40.4 (CH_2), 26.4 (CH_3), 22.2 (CH_3); HRMS (EI): Calcd. for $C_{10}H_{11}NO$: 161.0841; found: 161.0837; $[\alpha]_{20}^{D}$ = +262.6° (c = 3.3, $CHCl_3$); mp 58-59 °C.

(1*R*,3*R*,4a*S*,8a*S*)-7,9,9-Trimethyl-4-oxo-1,3,4,5,8,8a-hexahydro-2*H*-1,3-methano-naphthalene-4a-carbonitrile



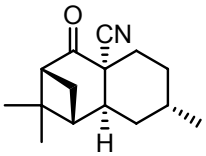
(+)-5

To a 50 mL 2-neck round bottom flask was placed $ZnCl_2$ (544 mg, 4.0 mmol). This was heat-fused to give a clear colorless melt and cooled to rt. Anhydrous CH_2Cl_2 (15 mL) was added and the mixture stirred until a fine suspension was formed (a spatula was used to crush the big pieces to facilitate this process). A solution of compound **4** (322 mg, 2.0 mmol) in anhydrous CH_2Cl_2 (5 mL) was added dropwise and the cloudy mixture stirred for 30 min, at which time a clear solution was obtained. Isoprene (2.7 mL, 20 mmol) was introduced and the resulting reaction mixture was stirred for 48 h at rt. Water was added to quench the reaction, and the aqueous layer was separated and extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to afford the crude product which was purified by flash chromatography (*n*-hexane:ethyl acetate = 20:1) to give compound (+)-**5** (384 mg, 84%) as a white solid.

IR (neat, cm^{-1}): 2236 (CN), 1715 (C=O) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ

5.73 (bs, 1H), 2.78 (t, *J* = 6 Hz, 1H), 2.72 (t, *J* = 4.0 Hz, 1H), 2.68 (td, *J* = 4, 1.6 Hz, 1H), 2.51~2.56 (m, 1H), 2.19 (t, *J* = 6.0 Hz, 1H), 2.11~2.16 (m, 2H), 1.93~1.96 (m, 1H), 1.83 (bs, 3H), 1.75 (d, *J* = 9.2 Hz, 1H), 1.38 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 205.7 (C), 138.6 (C), 122.7 (C), 118.9 (CH), 56.5 (CH), 47.5 (CH), 41.4 (C), 37.9 (CH), 35.0 (CH_2), 32.2 (CH_2), 25.9 (CH_3), 23.7 (CH_2), 23.1 (CH_3), 22.2 (CH_3); HRMS (EI): Calcd. for $C_{15}H_{19}NO$: 229.1467; found: 229.1466; $[\alpha]_{20}^{D}$ = +81.0° (c = 2.5, $CHCl_3$); mp 100-10 °C.

(1*R*,3*R*,4a*S*,7*S*,8a*S*)-7,9,9-Trimethyl-4-oxo-octahydro-1,3-methano-naphthalene-4a-carbonitrile

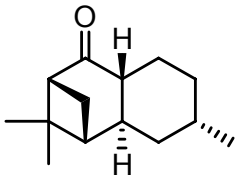


(+)-14

A black suspension of compound (+)-**5** (300 mg, 1.3 mmol) and 20% Pd/C (60 mg) in EtOH (10 mL) was shaken under an atmosphere of hydrogen (30 psi) for 30 h at rt. The reaction mixture was filtered through Celite® and the residue was rinsed with ethyl acetate (2 x 10 mL). The filtrate was concentrated *in vacuo* to give the crude product which was purified by flash chromatography (*n*-hexane:ethyl acetate = 20:1) to afford compound (+)-**14** (252 mg, 91%) as a colorless oil.

IR (neat, cm^{-1}): 2234 (CN), 1720 (C=O) cm^{-1}; ^{l}H NMR (400 MHz, $CDCl_3$): δ 2.62 (t, *J* = 5.6 Hz, 1H), 2.59 (d, *J* = 8.0 Hz, 1H), 2.48~2.54 (m, 1H), 2.11~2.15 (m, 1H), 2.05 (t, *J* = 4.8 Hz, 1H), 1.88~1.97 (m, 3H), 1.46~1.64 (m, 3H), 1.31 (s, 3H), 1.16~1.26 (m, 1H), 0.85 (dd, *J* = 11.2, 4.8 Hz , 3H) 0.81(s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 205.2 (C), 121.1 (C), 56.5 (CH), 48.2 (CH), 45.5 (C), 43.4 (C), 36.3 (CH_2), 35.8 (CH), 34.3 (CH_2), 30.0 (CH_2), 26.5 (CH_3), 25.7 (CH), 25.3 (CH_2), 22.6 (CH_3), 21.8 (CH_3); HRMS (EI): Calcd. for $C_{15}H_{21}NO$: 231.1623; found: 231.1626; $[\alpha]_{20}^{D}$ = +60.4° (c = 6.7, $CHCl_3$).

(1*R*,3*R*,4a*R*,7*S*,8a*S*)-7,9,9-Trimethyl-octahydro-1,3-methano-naphthalen-4-one

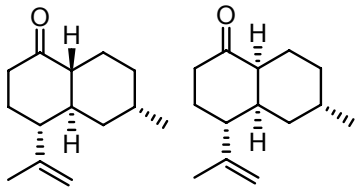


(+)-12

To a solution of compound (+)-**14** (160 mg, 0.69 mmol) in THF (6 mL) at -78 °C was added dropwise a precooled (-78 °C) 0.98M solution of LN in THF until the color of the reaction mixture remained deep green (2.01 mmol of LN was used). After stirring at -78 °C for 1 h, the mixture was warmed to room temperature and an aqueous saturated solution of NH_4Cl was added. The separated aqueous layer was extracted with ethyl acetate (2 x 15 mL) and the combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product thus obtained was purified by flash chromatography (*n*-hexane:ethyl acetate = 40:1) to afford compound (+)-**12** (120 mg, 86%) as a colorless oil.

IR (neat, cm^{-1}): 1712 (C=O) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.47 (dd, *J* = 5.4, 5.4 Hz, 1H), 2.34 (ddd, *J* = 10.8, 7.2, 5.4 Hz, 1H), 2.07~2.10 (m, 2H), 1.81~1.92 (m, 4H), 1.78 (d, *J* = 10.8 Hz, 1H), 1.45~1.64 (m, 3H), 1.31~1.39 (m, 3H), 1.30 (s, 3H), 0.98 (d, *J* = 7.2 Hz, 1H), 0.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.9 (C), 58.2 (CH), 50.8 (CH), 45.8 (CH), 44.9 (C), 37.7 (CH_2), 33.6 (CH), 32.0 (CH_2), 28.2 (CH), 26.7 (CH_3), 24.4 (CH_2), 21.8 (CH_3), 19.5 (CH_2), 19.3 (CH_3); HRMS (EI): Calcd. for $C_{14}H_{22}O$: 206.1672; found: 206.1666. $[\alpha]_{20}^{D}$ = +66.7° (c = 1.7, $CHCl_3$).

(4*R*,4aS,6*S*,8a*R*)-4-Isopropenyl-6-methyl-octahydro-naphthalen-1-one & (4*R*,4a*S*,6*S*,8a*S*)-4-Isopropenyl-6-methyl-octahydro-naphthalen-1-one



(-)-6 **(+)-17**

Ethylene glycol (0.6 mL, 11.0 mmol) and *p*-toluenesulfonic acid (230 mg, 1.2 mmol) were added to a solution of compound (+)-**12** (255 mg, 1.25 mmol) in benzene (60 mL). A Dean-Stark apparatus was fitted onto the reaction flask for azeotropic

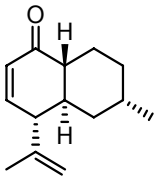
removal of water and the reaction mixture was refluxed for 48 h. The remaining benzene layer cooled to rt and washed with 1M $NaOH_{(aq)}$ solution and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The reaction product thus obtained was, without further purification, dissolved in acetone-water (10:1, 15 mL) containing a small amount of *p*-toluenesulfonic acid (76 mg, 0.4 mmol) and the solution mixture was refluxed for 3 h, cooled to rt,, the volatiles removed, and the remaining residue dissolved in ethyl acetate (20 mL). This was then washed with 1M $NaOH_{(aq)}$ and brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude product thus obtained was chromatographed over silica gel (*n*-hexane:ethyl acetate = 40:1) to afford compound (-)-**6** (137 mg, 54%) as a white solid along with compound (+)-**17** (94 mg, 37%) as a colorless oil.

Compound (-)-**6**: IR (neat, cm^{-1}): 1712 (C=O), 1640 (C=C) cm^{-1}: ^1H NMR (400 MHz, $CDCl_3$): δ 4.75 (m, 2H), 2.36~2.40 (m, 2H), 2.18 (ddd, *J* = 12.0, 10.8, 4.0 Hz, 1H), 1.88~1.96 (m, 3H), 1.42~1.82 (m, 10H), 1.20 (td, *J* = 12.0, 4.8 Hz, 1H), 0.90 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.5 (C), 146.1 (C), 111.9 (CH_2), 53.9 (CH), 51.1 (CH), 41.0 (CH_2), 39.5 (CH), 37.5 (CH_2), 32.1 (CH_2), 30.2 (CH_2), 26.7 (CH), 19.2 (CH_2), 18.1 (CH_3), 17.2 (CH_3); HRMS (EI): Calcd. for $C_{14}H_{22}O$: 206.1672; found: 206.1670; $[\alpha]_{20}^{D}$ = -11.12° (c = 0.8, $CHCl_3$); mp 71-72 °C.

Compound (+)-**17**: IR (neat, cm^{-1}): 1710 (C=O),1640 (C=C) cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 4.75(m, 2H), 2.68 (td, *J* = 9.6, 3.6 Hz, 1H), 2.51 (td, *J* = 14.4, 6.0 Hz, 1H), 2.34 (ddd, *J* = 12.6, 6.8, 3.6 Hz, 1H), 2.20~2.24 (m, 1H), 1.93~1.97 (m, 1H), 1.83~1.87 (m, 1H), 1.47~1.72 (m, 9H), 0.80~0.91 (m, 2H), 0.78 (d, *J* = 9.6 Hz, 3H): ^{13}C NMR (150 MHz, $CDCl_3$): δ 215.0 (C), 146.5 (C), 112.3 (CH_2), 52.5 (CH), 42.3 (CH), 38.8 (CH), 37.8 (CH_2), 36.1 (CH_2), 34.2 (CH_2), 31.5 (CH_2), 26.0 (CH_2), 26.0 (CH), 22.7 (CH_3), 18.0 (CH_3)； HRMS (EI): Calcd. for $C_{14}H_{22}O$: 206.1672; found: 206.1669; $[\alpha]_{20}^{D}$ = +106.8 ° (c = 1.2, $CHCl_3$).

Epimerization of (+)-**17** to (-)-**6:** Compound (+)-**17** (55 mg, 0.27 mmol) was dissolved in methanol (10 mL) and 3M $NaOH_{(aq)}$ (3.5 mL) was added to the solution. The mixture was refluxed for 22 h, cooled to rt, and extracted with ethyl acetate. The organic layers were combined, washed with water, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to give a mixture of (-)-**6**and (+)-**17** (41 mg, 74%, 3:1 ratio by ^1H nmr integration).

(4*R*,4a*S*,6*S*,8a*R*)-4-Isopropenyl-6-methyl-4a,5,6,7,8,8a-hexahydro-4*H*-naphthalen-1-one

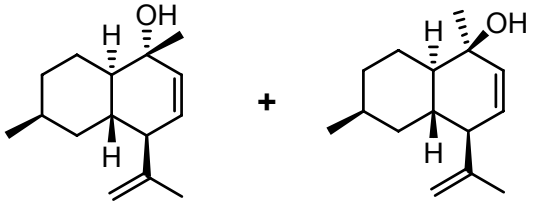


(-)-18

To a solution of anhydrous diisopropylamine (0.11 mL, 0.70 mmol) in ahydrous THF (5 mL) at 0 °C under a nitrogen atmosphere, was added *n*-BuLi (2.2M solution, 0.35 mL, 0.78 mmol) slowly. The mixture was stirred at 0 °C for 30 min and then cooled to -78 °C. A solution of (-)-**6** (80 mg, 0.39 mmol) in anhydrous THF (5 mL) was introduced dropwise, and the resulting mixture was stirred for 1 h, at which time a solution of diphenyl diselenide (157 mg, 0.70 mmol) in anhydrous THF (3 mL) was added. The reaction mixture was allowed to warm to rt and stirred for 24 h. Water was added and the quenched reaction mixture was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extracts were chilled to 0 °C and treated with 35% H_2O_2 (0.08 mL, 0.78 mmol). When no more starting material was detected by TLC, water was added and the separated aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extracts were washed with water and brine, dried over anhydrous MgSO4, filtered, and concentrated *in vacuo.* The crude product thus obtained was purified by chromatography on silica gel (ethyl acetate:*n*-hexane = 1:30) to furnish compound (-)-**18** (57 mg, 72%) as a colorless oil.

IR (neat, cm^{-1}): 1674 (C=O), 1645 (C=C) cm^{-1}: ^1H NMR (400 MHz, $CDCl_3$): δ 6.60 (dt, *J* = 10, 2 Hz, 1H), 5.94 (dt, *J* = 10.0, 2.4 Hz, 1H), 4.85 (d, *J* = 1.6 Hz, 1H), 4.78 (bs, 1H), 2.77 (d, *J* = 16.0 Hz, 1H), 1.87~2.01 (m, 4H), 1.52~1.59 (m, 6H), 1.29~1.37 (m, 1H), 1.18~1.28 (m, 1H), 0.87 (dd, *J* = 7.2, 2.4 Hz, 3H)； ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.9 (C), 152.8 (CH), 144.4 (C), 129.1 (CH), 114.1 (CH_2), 52.2 (CH), 50.5 (CH), 36.7 (CH), 36.6 (CH_2), 30.4 (CH_2), 26.5 (CH), 19.5 (CH_2), 19.3 (CH_3), 17.3 (CH_3); HRMS (EI): Calcd. for $C_{14}H_{20}O$: 204.1514; found: 204.1515; $[\alpha]_{20}^{D}$ = - 40.5° (c = 0.2, $CHCl_3$).

(1*R*,4*R*,4a*S*,6*S*,8a*R*)-4-Isopropenyl-1,6-dimethyl-1,4,4a,5,6,7,8,8a-octahydronaphthalen-1-ol and xenitorin C



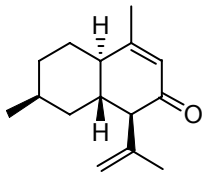
19 (-)-**2**

To a solution of $CeCl_3$ (18 mg, 0.07 mmol) in anhydrous THF (2 mL) at -78 °C under a blanket of nitrogen, was added a solution of compound (-)-**18** (30 mg, 0.15 mmol) in THF (2 mL) dropwise. The mixture was stirred at -78 °C for 20 min and then warmed to 0°C, at which time methyllithium (1.5M solution, 0.2 mL, 0.3 mmol) was introduced . After 4 h at 0 °C, water was added, and the separated aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL) and the combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. Chromatography of the crude product thus obtained using *n*-hexane and ethyl acetate in a ratio of 30:1 as eluting solvent afforded, individually, xenitorin C ((-)-**2**) (11 mg, 34%) as a colorless oil and compound **19** (19 mg, 58%) as a white solid.

Xenitorin C ((-)-**2**): IR (neat, cm^{-1}): 3436 (OH); ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.67 (dd, *J* = 10.2, 1.8 Hz, 1H), 5.46 (dd, *J* = 10.2, 1.8 Hz, 1H), 4.77 (d, *J* = 1.2 Hz, 1H), 4.71 (d, *J* = 1.8 Hz, 1H), 2.35 (dt, *J* = 9.6, 1.8 Hz, 1H), 1.94~1.97 (m, 1H), 1.50~1.73 (m, 10H), 1.23 (s, 3H), 1.13~1.15 (m, 1H), 1.08 (dt, *J* = 12.6, 4.8 Hz, 1H), 0.94 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.5 (C), 134.5 (CH), 132.6 (CH), 112.7 (CH_2), 68.5 (C), 52.6 (CH), 47.5 (CH), 36.9 (CH_2), 31.3 (CH_2), 29.2 (CH), 27.2 (CH_3), 27.1 (CH), 18.8 (CH_3), 18.8 (CH_2), 17.5 (CH_3); HRMS (EI): Calcd. for $C_{15}H_{24}O$: 220.1827; found: 220.1829; $[\alpha]_{20}^{D}$ = -4.6° (c = 0.7, $CHCl_3$).

Compound **19**: IR (neat, cm^{-1}): 3432 (OH); ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.61 (dd, *J* = 10.2, 2.4 Hz, 1H), 5.32 (dd, *J* = 10.2, 2.4 Hz, 1H), 4.77 (td, *J* = 3.0, 1.2 Hz, 1H), 4.70 (d, *J* = 1.2 Hz, 1H), 2.43 (td, *J* = 9.6, 2.4 Hz, 1H), 1.96~1.99 (m, 1H), 1.69~1.79 (m, 2H), 1.49~1.64 (m, 6H), 1.54 (s, 3H), 1.38~1.42 (m, 1H), 1.29~1.36 (m, 1H), 1.10~1.14 (m, 1H), 0.94 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.4 (C), 136.0 (CH), 129.8 (CH), 112.7 (CH_2), 71.8 (C), 52.7 (CH), 49.6 (CH), 37.4 (CH_2), 32.0 (CH), 31.2 (CH_2), 27.2 (CH), 23.8 (CH_3), 19.2 (CH_2), 18.7 (CH_3), 17.6 (CH_3); HRMS (EI): Calcd. for $C_{15}H_{24}O$: 220.1827; found:220.1824.

(1*R*,4a*R*,7S,8a*R*)-1-Isopropenyl-4,7-dimethyl-4a,5,6,7,8,8a-hexahydro-1*H*-naphthalen-2-One (Xenitorin B)



(-)-1

To a mixture of compound **19** (15 mg, 0.07 mmol) and Celite® (30 mg) in anhydrous CH_2Cl_2 (4 mL), was added pyridinium chlorochromate (30 mg, 0.14 mmol) in one portion at rt. The reaction mixture was stirred at rt for 4 h, diluted with CH_2Cl_2 (10 mL), and filtered through a pad of Celite®. After rinsing the Celite® pad with copious amounts of CH_2Cl_2, the filtrate was concentration under reduced pressure and the crude product thus obtained was purified by chromatography over silica gel (*n*-hexane:ethyl acetate = 30:1) to furnish xenitorin B ((-)-**1**) (11 mg, 73%) as a white solid. Alternatively, under similar reaction conditions xenitorin C ((-)-**2**) was transformed into xenitorin B ((-)-**1**) in 69% yield.

IR (neat, cm^{-1}): 2872,1666 (C=O); ^1H NMR (600 MHz, $CDCl_3$): δ 5.89 (q, J = 1.2 Hz, 1H), 5.00 (s, 1H), 4.75 (s, 1H), 2.67 (d, J = 12.0 Hz, 1H), 1.90~2.05 (m, 7H), 1.56~1.63 (m, 5H), 1.46 (br d, J = 12.6 Hz, 1H), 1.23~1.36 (m, 2H), 0.95 (d, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 198.8 (C), 164.1 (C), 141.2 (C), 127.2 (CH), 116.6 (CH_2), 62.2 (CH), 45.6 (CH), 36.6 (CH_2), 36.5 (CH), 31.7 (CH_2), 26.7 (CH), 23.4 (CH_2), 21.4 (CH_3), 18.4 (CH_3), 17.7 (CH_3); HRMS (EI): Calcd. for $C_{15}H_{22}O$: 218.1671; found: 218.1670; $[\alpha]_{20}^{D}$ = - 5.3° (c = 1.8, $CHCl_3$).