Supporting Information

Icetexane Diterpenoids from Perovskia atriplicifolia

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S1 Extraction and isolation

The air-dried whole *Perovskia atriplicifolia* plants (9.0 kg) were powdered and extracted with 90% ethanol (54 L) under reflux three times, 2 hours each time. After being concentrated *in vacuo*, the extract was suspended in water and successively partitioned with petroleum ether, chloroform, and n-BuOH to give petroleum ether (A), chloroform (B), n-BuOH (C), and aqueous (D) fractions.

The petroleum ether (A) (260 g) extract was subjected to silica gel (2.0 kg; 200-300 mesh; 10 × 170 cm) chromatography column (CC) and eluted with gradient petroleum ether/acetone (100:0, 98:2, 95:5, 90:10, 80:20; v/v; each 5.0 L; fraction size: 1000 mL/flask; flow rate: 5 mL/min) to afford six fractions (Frs.A.1-6). The Fr.A.2 (5.6 g, eluted by petroleum ether/acetone 98:2) was performed on silica gel CC (270 g; 200-300 mesh; 3 × 50 cm; petroleum ether/acetone 100:0, 99:1, 98:2; v/v; each 1.0 L; fraction size: 500 mL/flask; flow rate: 2 mL/min) to afford four subfractions (Frs.A.2.1-2.4). Fr.A.2.2 (1.32 g) was subjected to an MCI CC (80 g; 2 × 35 cm; MeOH/H$_2$O 70:30, 80:20, 90:10, 100:0; each 1.0 L; fraction size: 100 mL/flask; flow rate: 2 mL/min) to give four subfractions (Frs. A.2.2.1-2.2.4). Fr.A.2.2.4 (350 mg) was purified by HPLC with an eluent of CH$_3$CN/H$_2$O (40:60; v/v; 2 ml/min) to yield compounds 1 (23 mg; purity > 94 %, HPLC, $R_t = 21.7$ min) and 7 (72 mg; purity > 95%, HPLC, $R_t = 32.5$ min). Fr.A.3 (26.3 g, eluted by petroleum ether/acetone 95:5) was separated on a silica gel CC (1.2 kg; 200-300 mesh; 8 × 100 cm), eluting with gradient petroleum ether/EtOAc (98:2, 95:5, 90:10; v/v; each 2.0 L, fraction size: 1000 mL/flask; flow rate: 4 mL/min) to provide four fractions (Fr.A.3.1- Fr.A.3.4). Fr.A.3.4 (0.21 g) was subjected to Rp-18 CC (75 g; 2 × 35 cm; MeOH/H$_2$O 70:30; 100 ml per fraction), followed by purification on HPLC (CH$_3$CN/H$_2$O 40:60; 2 ml/min) to give compounds 3 (16 mg, purity > 96%, HPLC, $R_t = 17.3$ min), 4 (4.8 mg, purity > 96%, HPLC, $R_t = 22.1$ .....
min), and 6 (40 mg, purity > 95%, HPLC, \( R_t = 35.5 \) min). Fr.A.5 (6.2 g, eluted by petroleum ether/acetone 90:10) was decolored on an MCI CC (250 g, 3 × 500 cm; MeOH/H\(_2\)O 40:60, 60:40, 80:20, 90:10, 100:0; each 800 ml; fraction size: 200 mL/flask; flow rate: 2 mL/min) to give five subfractions (Frs.A.5.1-5.5). Fr.A.5.3 (0.8 g) was further purified by Rp-18 (75 g, 2 × 35 cm; MeOH/H\(_2\)O 75: 25; 100 ml per fraction) to give three fractions (Frs.A.5.3.1-5.3.3). Fr.A.5.3.2 (153 mg) was partitioned on a Sephadex LH-20 (200 g, 1 × 160 cm; MeOH/CHCl\(_3\) 1:1) to yield compound 2 (44 mg). Fr.A.5.3.3 (365 mg) was purified by HPLC (CH\(_3\)CN/H\(_2\)O 38: 62; 2 ml/min) to give compounds 5 (3.2 mg, purity > 93%, HPLC, \( R_t = 31.5 \) min) and 8 (113 mg, purity > 96%, HPLC, \( R_t = 48.2 \) min).
$2\text{S}^1\text{H NMR (400 MHz) spectrum of compound 1 in CD}_3\text{OD.}$
$^{38}$\(^{13}\)C NMR (100 MHz) spectrum of compound 1 in CD$_3$OD.
Enlarged $^{13}$C NMR (400 MHz) spectrum of compound 1 in CD$_3$OD.
4S HSQC spectrum of compound 1 in CD$_3$OD.
$^5$H HMBC spectrum of compound 1 in CD$_3$OD.
Enlarged HMBC spectrum of compound 1 in CD$_3$OD.
$^6S\ H^1H$ COSY spectrum of compound 1 in CD$_3$OD.
7S ROESY spectrum of compound 1 in CD$_3$OD.
$^1$H NMR (400 MHz) spectrum of compound 2 in CD$_3$OD.
8S Enlarged $^1$H NMR (400 MHz) spectrum of compound 2 in CD$_2$OD.
$^{13}$C NMR (100 MHz) spectrum of compound 2 in CD$_3$OD.
Enlarged $^{13}$C NMR (100 MHz) spectrum of compound 2 in CD$_3$OD.

C$_{13}$CPD

ppm
10S HSQC spectrum of compound 2 in CD$_3$OD.
11S HMBC spectrum of compound 2 in CD$_3$OD.
12S ROESY spectrum of compound 2 in CD$_3$OD.
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$J = 2.4$
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29S ROESY spectrum of compound 5 in CD$_3$OD.
$^{30}$Si $^1$H NMR (400 MHz) spectrum of compound 6 in CD$_3$OD.
$^{31}$Cl NMR (100 MHz) spectrum of compound 6 in CD$_3$OD.
Enlarged $^{13}$C NMR (100 MHz) spectrum of compound 7 in CD$_3$OD.

$J = 3.4$
$^{32}$S HSQC spectrum of compound 6 in CD$_3$OD.
HMBC spectrum of compound 6 in CD$_3$OD.