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Short communication

Three new 18,19-*seco*-ursane glycosides from *Elsholtzia bodinieri*

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ABSTRACT

Chromatographic separation of an extract of the aerial part of *Elsholtzia bodinieri* resulted in the isolation of three new 18,19-*seco*-ursane glycosides, bodiniosides E-G (**1**–**3**). Their structures were elucidated as 2α,12β,23-trihydroxy-3-(β-D-glucopyranosyl)-19-oxo-18,19-*seco*-urs-13(18)-en-28-*O*-β-D-glucopyranosyl ester (**1**), 3-β-D-glucopyranosyl-19-β-D-glucopyranosyl-12β,21-dihydroxy-18,19-*seco*-urs-13(18)-en-28-oic acid (**2**), and 2α,12β,21-trihydroxy-3-β-D-glucopyranosyl-19-β-D-glucopyranosyl-18,19-*seco*-urs-13(18)-en-28-oic acid (**3**), respectively, by extensive NMR techniques, including 1D- and 2D-NMR experiments, as well as comparing with spectral data with those of the known analogues.

1. Introduction

The species *Elsholtzia bodinieri* Vaniot, belonging to the genus *Elsholtzia* (Labiatae), is an annual herbaceous plant distributed in Yunnan and Guizhou Provinces in China. It is generally known as "Dongzisu" and used as herbal tea or folk medicine for the treatment of cough, headache, pharyngitis, fever and hepatitis (Jiangsu New Medical College, 1985). Previous phytochemical studies on *E. bodinieri* showed that this plant was a rich source of triterpenoids, diterpenoids and flavonoids as well as their corresponding glycosides, including oleanane triterpenoid saponins (Zhu et al., 2002; Hu et al., 2007; Li et al., 2012), 18,19-*seco*-ursane monodesmoside saponins (Li et al., 2005), clerodane diterpenoid glycosides (Hu et al., 2008), flavonoid and flavanone glycosides (Li et al., 2008). With an aim to discover more new compounds from *E. bodinieri*, we further systematically investigated the *n*-BuOH soluble fraction of this plant, which led to the isolation of three new 18,19-*seco*-ursane glycosides, bodiniosides E-G (**1**–**3**). We report herein the isolation and structural elucidation of the isolates.

2. Results and discussion

Compound **1**, $[\alpha]_D^{19.3}$ −29.05 (c 0.19, MeOH), white amorphous powder, gave rise to a quasi-molecular ion peak at *m*/*z* 867.4117 ([M + Na]$^+$) in the HR-ESI-MS, which corresponded to the molecular formula $C_{42}H_{68}O_{17}$, and was further confirmed by its ^{13}C NMR and DEPT analysis. The IR absorption bands indicated the existence of hydroxyl groups (3428 cm^{-1}), carbonyl groups (1734 and 1701 cm^{-1}), and olefinic functional groups (1636 cm^{-1}). The ^{1}H NMR spectrum (Table 1) of **1** revealed six methyl signals at δ_H 1.35 (3H, s, Me-24), 0.74 (3H, s, Me-25), 1.03 (3H, s, Me-26), 1.17 (3H, s, Me-27), 2.06 (3H, s, Me-29), and 0.96 (3H, d, *J* = 6.6 Hz, Me-30), three oxygen-bearing methines at δ_H 4.09 (1H, m, H-2), 3.28 (1H, d, *J* = 9.1 Hz, H-3) and 4.56 (1H, dd, *J* = 1.5, 10.0 Hz, H-12), as well as an olefinic proton at δ_H 6.54 (1H, s, H-18). In addition, a series of typical signals of two sugar residues were recognized, including two anomeric proton signals at δ_H 4.93 (1H, d, *J* = 7.8 Hz, H-1′) and 6.32 (1H, d, *J* = 8.2 Hz, H-1″), revealing β-configuration present in both sugar residues on the basis of their $^3J_{H1,H2}$ coupling constants (Zhang et al., 2012) Fig. 1. On acid hydrolysis of **1**, only D-glucose (Glc) was detected as sugar residues by GC chromatography with the corresponding trimethylsilylated L-cysteine derivatives. Except for the signals belonging to the glucosyl groups, the ^{13}C NMR and DEPT spectra (Table 2) of **1** exhibited resonances for 30 carbons, including eight quaternary carbons (two are carbonyls at δ_C 211.8 and 175.3 and an olefinic carbon at δ_C 147.6), seven methines containing three oxygenated ones (δ_C 66.9, d, C-2; 95.4, d, C-3; 69.1, d, C-12) and an olefinic one (δ_C 120.9, d, C-18), nine methylenes including an oxygenated one (δ_C 63.9, t, C-23), and six methyls (δ_C 18.1, q, C-24; 17.8, q, C-25; 18.1, q, C-26; 21.6, q, C-27; 28.5, q, C-29; 16.3, q, C-30), which were assigned to 18, 19-*seco*-ursane triterpene skeleton (Li et al., 2005; Kakuno et al., 1991). Careful comparison of the ^{1}H and ^{13}C NMR data of **1** with those of laevigin B (Yan et al., 2013) suggested their structural similarities, except for the presence of an additional Glc moiety in **1**. The glycosidic linkages at C-3 and C-28 of the aglycone were determined by the HMBC correlations (Fig. 2) from H-1′ to C-3, from H-3 to C-1′, and from H-1″ to C-28, respectively. Furthermore, the chemical shift (δ_C 96.4, d, C-1") of the anomeric carbon appeared in upfield further

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Table 1
^{1}H NMR data of compounds **1–3** in pyridine-d_5 (600 MHz, δ_H, mult, J in Hz).

No.	1	2	3
1	1.18 (overlap)	1.75 (overlap)	1.17 (overlap)
	2.39 (m)	0.95 (m)	2.40 (m)
2	4.09 (m)	2.03 (m)	4.07 (m)
	–	2.12 (m)	–
3	3.28 (d, 9.1)	3.40 (dd, 4.4, 11.7)	3.29 (d, 9.2)
5	0.95 (m)	0.84 (m)	0.89 (m)
6	1.47 (m)	1.48 (m)	1.45 (m)
	1.27 (m)	1.19 (m)	1.14 (m)
7	1.43 (m)	1.39 (m)	1.44 (m)
	1.20 (overlap)	1.20 (overlap)	1.20 (overlap)
9	1.60 (d, 9.2)	1.61(br s)	1.62 (br s)
11	2.28 (m)	2.31(m)	2.33 (m)
	1.62 (m)	1.61(m)	1.60 (m)
12	4.56 (dd, 1.5, 10.0)	4.47 (dd, 2.1, 11.7)	4.67 (dd, 2.2, 10.7)
15	1.10 (m)	1.02 (m)	1.01 (m)
	2.28 (m)	2.47 (m)	2.36 (m)
16	1.63 (m)	1.64 (m)	1.63 (m)
	1.94 (m)	1.86 (m)	1.86 (m)
18	6.54 (s)	6.45 (s)	6.43 (s)
19	–	4.30 (m)	4.26 (m)
20	2.42 (m)	2.05 (m)	2.30 (m)
21	1.73 (m)	4.66 (m)	4.67 (m)
	2.20 (m)	–	–
22	1.70 (m)	1.72 (m)	1.70 (m)
	2.52 (d, 12.6)	2.35 (dd, 6.9, 13.3)	2.33 (dd, 6.9, 13.0)
23	3.35 (d, 9.0)	1.11(s)	1.19 (s)
	4.45 (m)	–	–
24	1.35 (s)	1.31(s)	1.36 (s)
25	0.74 (s)	0.79 (s)	0.83 (s)
26	1.03 (s)	0.95 (s)	0,97 (s)
27	1.17 (s)	1.25 (s)	1.08 (s)
29	2.06 (s)	1.27 (d, 6.4)	1.26 (d, 6.8)
30	0.96 (d, 6.6)	0.93 (d, 6.9)	0.91 (d, 6.3)
3-Glc			
1′	4.93 (d, 7.8)	4.95 (d, 8.1)	4.94 (d, 7.8)
2′	4.10 (overlap)	4.05 (m)	4.06 (m)
3′	4.20 (m)	4.40 (m)	4.27 (m)
4′	4.14 (m)	4.38 (m)	4.37 (m)
5′	4.31 (m)	4.31 (m)	4.31 (m)
6′	4.32 (dd, 4.7, 12.1)	4.37 (dd, 4.8, 11.8)	4.33 (dd, 4.7, 11.8)
	4.50 (m)	4.65 (m)	4.45 (m)
19-Glc			
H-1″		4.88 (d, 7.8)	4.84 (d, 7.7)
H-2″		3.98 (m)	3.98 (m)
H-3″		4.20 (m)	4.16 (m)
H-4″		4.41 (m)	4.26 (m)
H-5″		3.86 (ddd, 2.5, 4.7, 9.3)	3.95 (m)
H-6″		4.24 (m)	4.59 (m)
28-Glc			
H-1″	6.32 (d, 8.2)		
H-2″	4.21 (m)		
H-3″	4.18 (m)		
H-4″	4.39 (m)		
H-5″	4.00 (m)		
H-6″	4.01 (m)		
	4.24 (m)		

supported the existence of ester glycoside at C-28 (Laura et al., 2012).

The relative configuration of **1** was determined through inspection of the ROESY spectrum. The NOE correlation between Me-24 and Me-25 indicated the α-orientation of the hydroxymethylene group at C-23. Additionally, the ROESY cross-peaks of H-2/Me-25 and H-3/H-5 established the β-orientation of H-2 and α-orientation of H-3, respectively. Based on the above evidence, the structure of **1** was established as 2α,12β,23-trihydroxy-3-(β-D-glucopyranosyl)-19-oxo-18,19-*seco*-urs-13(18)-en-28-*O*-β-D-glucopyranosyl ester, and named bodinioside E.

Compound **2**, $[\alpha]_D^{19.3}$ −88.97 (c 0.09, MeOH + $CHCl_3$ 2:1), was obtained as white amorphous powder and its molecular formula was determined as $C_{42}H_{70}O_{16}$ on basis of the quasi-molecular ion

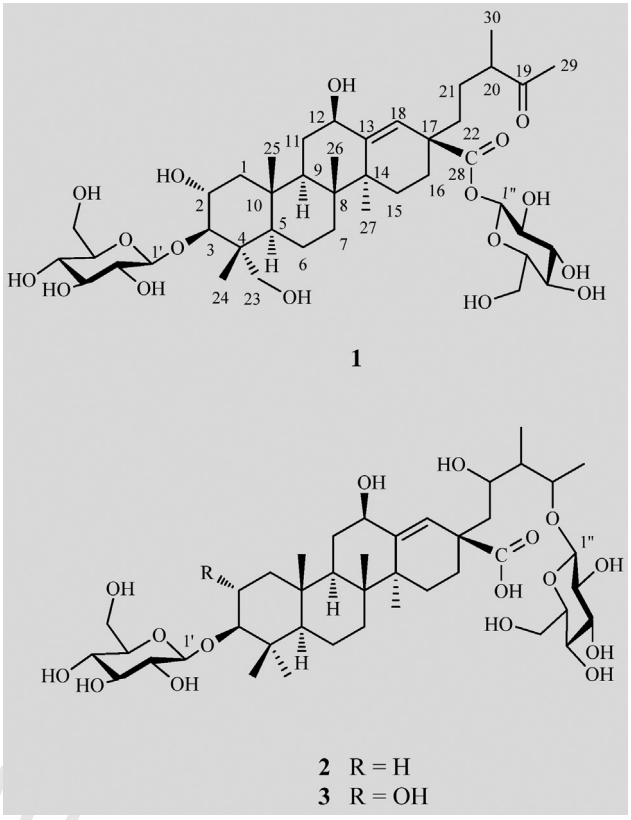


Fig. 1. Structures of compounds **1–3**.

observed at m/z 811.4470 (HR-ESI-MS, $[M–H_2O–H]^-$), consistent with a molecular formula of $C_{42}H_{70}O_{16}$ assigned by a combinational analysis of ^{1}H, ^{13}C NMR and DEPT spectra. The ^{1}H NMR spectrum (Table 1) of **2** showed seven methyl signals at δ_H 1.11 (3H, s, Me-23), 1.31 (3H, s, Me-24), 0.79 (3H, s, Me-25), 0.95 (3H, s, Me-26), 1.25 (3H, s, Me-27), 1.27 (3H, d, J = 6.4 Hz, Me-29), and 0.93 (3H, d, J = 6.9 Hz, Me-30), four oxygen-bearing methines at δ_H 3.40 (1H, dd, J = 4.4, 11.7 Hz, H-3), 4.47 (1H, dd, J = 2.1, 11.7 Hz, H-12), 4.30 (1H, m, H-19) and 4.66 (1H, m, H-21), and an olefinic proton at δ_H 6.45 (1H, s, H-18). In addition, the presence of two anomeric signals at δ_H 4.95 (1H, d, J = 8.1 Hz, H-1′) and 4.88 (1H, d, J = 7.8 Hz, H-1″) revealed the existence of two sugar residues with β-configuration (Zhang et al., 2012). Acid hydrolysis of **2** afforded D-glucose (Glc) as sugar residues, which was confirmed by GC analysis of their corresponding trimethylsilylated L-cysteine derivatives. In addition to the sugar moieties, the ^{13}C NMR spectrum (Table 2) showed the presences of one carbonyl (δ_C 179.1, s, C-28), seven methyls (δ_C 17.1, q, C-23; 28.2, q, C-24; 16.9, q, C-25; 18.5, q, C-26; 22.1, q, C-27; 22.0, q, C-29; 8.8, q, C-30), eight methylenes, eight methines (four oxygenated ones at δ_C 88.8, 68.1, 76.6, 77.5, and one olefinic one at δ_C 116.9), seven quaternary carbons (one olefinic at δ_C 149.5). The ^{1}H- and ^{13}C NMR spectra closely matched with those of cornutaoside B, a known 18, 19-*seco*-ursane triterpene glycoside isolated from *Ilex cornuta* (Wu et al., 2008). The differences between compound **2** and cornutaoside B were the nature of the sugars, including the types and linkage of the sugar residues. HMBC correlations observed between H-1′ and C-3 (δ_C 88.8) of the aglycone, indicated that one Glc moiety was linked to C-3. Moreover, elaborative comparison of the NMR data of the aglycone of **2** with those of cornutaoside B exhibited that the chemical shift of C-19 in compound **2** obviously moved to downfield (from δ_C 68.4 in cornutaoside B to δ_C 76.6 in **2**), which suggested that the other Glc moiety was located at C-19. Furthermore, the HMBC

Table 2
^{13}C NMR data of compounds **1**–**3** in pyridine-d_5 (150 MHz).

No.	1	2	3
	δ_C	δ_C	δ_C
1	47.6 t	39.1 t	47.3 t
2	66.9 d	26.7 t	66.7 d
3	95.4 d	88.8 d	95.2 d
4	40.8 s	39.6 s	40.5 s
5	55.8 d	56.0 d	55.6 d
6	18.4 t	18.3 t	18.1 t
7	34.8 t	33.1 t	32.9 t
8	41.3 s	41.9 s	41.2 s
9	49.6 d	49.6 d	49.3 d
10	38.1 s	37.2 s	37.9 s
11	33.0 t	34.9 t	34.5 t
12	69.1 d	68.1 d	68.7 d
13	147.6 s	149.5 s	149.4 s
14	41.3 s	41.5 s	41.6 s
15	27.9 t	26.7 t	27.5 t
16	28.0 t	28.2 t	29.1 t
17	43.9 s	44.0 s	43.8 s
18	120.9 d	116.9 d	116.7 d
19	211.8 s	76.6 d	76.5 d
20	47.4 d	42.7 d	43.0 d
21	29.3 t	77.5 d	77.3 d
22	39.5 t	41.9 t	42.5 t
23	63.9 t	17.1 q	17.8 q
24	18.1 q	28.2 q	28.3 q
25	17.8 q	16.9 q	17.0 q
26	18.1 q	18.5 q	18.3 q
27	21.6 q	22.1 q	22.1 q
28	175.3 s	179.1 s	179.0 s
29	28.5 q	22.0 q	21.8 q
30	16.3 q	8.8 q	8.6 q
3-Glc			
1′	106.6 d	107.1 d	106.3 d
2′	75.6 d	75.8 d	75.4 d
3′	78.6 d	78.3 d	78.0 d
4′	71.6 d	71.5 d	71.3 d
5′	78.7 d	78.4 d	78.4 d
6′	62.6 t	62.7 t	62.4 t
Glc′			
1″		104.5 d	104.3 d
2″		75.4 d	75.1 d
3″		78.7 d	78.4 d
4″		71.9 d	71.4 d
5″		78.8 d	78.5 d
6″		63.1 t	62.5 d
28-Glc			
1″	96.4 d		
2″	74.0 d		
3″	78.8 d		
4″	71.2 d		
5″	79.4 d		
6″	62.4 t		

correlations from Me-29 and H-1″ to C-19 further confirmed the above conclusion. Thus, compound **2** was established as 3-β-D-glucopyranosyl-19-β-D-glucopyranosyl-12β,21-dihydroxy-18,19-*seco*-urs-13(18)-en-28-oic acid, and given the name bodinioside F.

Compound **3**, $[\alpha]_D^{19.3}$ −45.71 (c 0.32, MeOH), the molecular formula was determined to be $C_{42}H_{70}O_{17}$ as deduced by HR-ESI-MS at *m*/*z* 827.4424 ($[M-H_2O-H]^-$), indicating eight degrees of unsaturation. Detailed comparison of the ^{1}H- (Table 1) and ^{13}C NMR (Table 2) data of **3** with those of **2** revealed that they showed highly similarity except for the signals at C-1, C-2 and C-3, which indicated that compound **3** possessed different substitute mode in ring A. The chemical shift of C-2 evidently moved to low field suggested that the methylene at C-2 (δ_H 2.03, 2.12; δ_C 26.7, t) in **2** was substituted by a hydroxyl group in **3** (δ_H 4.07, δ_C 66.7, d). Moreover, the HMBC correlations (Fig. 2) from H-1 (δ_H 2.40, m) and H-3 (δ_H 3.29, d, J = 9.2 Hz) to C-2 further confirmed the above assignment. The relative configuration of **3** was established by analysis of the ROESY spectrum. NOE correlations of H-2/Me-25 and H-3/H-5 determined the β-oriented of H-2 and α-oriented of H-3, respectively. Therefore, the structure of bodinioside G (**3**) was assigned as 2α,12β,21-trihydroxy-3-β-D-glucopyranosyl-19-β-D-glucopyranosyl-18,19-*seco*-urs-13(18)-en-28-oic acid.

3. Experimental

3.1. General experimental procedures

1D and 2D NMR spectra were recorded using Bruker Avance III-600 instrument with tetramethylsilane (TMS) as an internal standard. ESI and HR-ESI-MS were taken on an API Qstar Pulsar instrument. Semi-preparative HPLC was performed on an Agilent 1200 liquid chromatograph with a ZORBAX SB-C18 (5 μm, 9.4 mm × 250 mm) column. Column chromatography (CC) was carried out on silica gel (200–300 mesh, 100–200 mesh, 80–100 mesh, Qingdao Marine Chemical Factory, Qingdao, China), Diaion HP-20SS (63–150 μm Mitsubishi Fine Chemical Industries Co., Ltd., Tokyo, Japan), ODS-C_{18} (75 μm, YMC Co., Ltd., Japan) and Sephadex LH-20 (Amersham Biosciences AB, Uppsala, Sweden). Fractions were monitored by TLC plates (Silica gel H, Qingdao Marine Chemical Factory, Qingdao, China), and spots were visualized by heating silica gel plates sprayed with 5% H_2SO_4–EtOH.

3.2. Plant material

The sample of *E. bodinieri* was collected from Honghe, Yunnan Province, PR China, in May 2008, and was identified by Prof. Hai-Zhou Li. A voucher specimen (KMUST 20080003) was deposited at the Laboratory of Phytochemistry, Faculty of Life Science and Technology, Kunming University of Science and Technology.

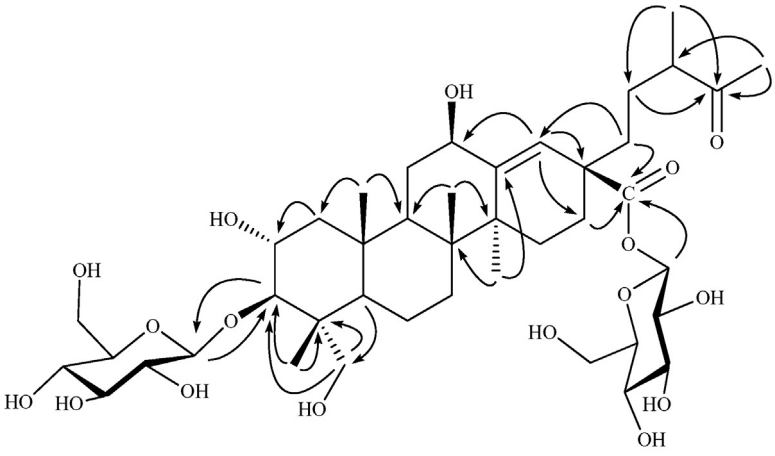
3.3. Extraction and isolation

The aerial parts of *E. bodinieri* (15.0 kg) were powdered and extracted with 75% Me_2CO (3 × 35 L, 48 h, each) at room temperature and filtered. The filtrate was concentrated in *vacuo* and the resulting residue was extracted successively with $CHCl_3$, EtOAc and *n*-BuOH, respectivley.

The *n*-BuOH extract (300.0 g) was separated over macroporous resin CC (110 × 1200 mm) eluting with MeOH/H_2O (gradient 10, 30, 60, 90, and 100%, each 2.5 L) to afford fractions I–IV. Fr. II (50 g) was Q6 subjected to Sephadex LH-20 gel CC, eluting with MeOH/H_2O (gradient 10, 30, 50, 70, 90, and 100%, each 1 L) and silica gel CC (chloroform/MeOH, gradient 20:1 → 0:1) to obtain subfractions II-1–II-4. Fr. II-4 (7.9 g) was chromatographed successively over silica gel CC (chloroform/MeOH/H_2O, gradient 20:1:0.1 → 5:5:0.5), ODS (MeOH/H_2O, gradient 10% → 100%), and semi-preparative HPLC (25% CH_3CN, 3 mL/min, t_R = 11.5 min) to obtain compound **1** (30.4 mg). Fr. II-3 (1.49 g) was purified over silica gel CC (chloroform/MeOH/H_2O, gradient 20:1:0.1 → 5:5:0.5), ODS (MeOH/H_2O, gradient 10% → 100%), and semi-preparative HPLC (29% CH_3CN, 3 mL/min, t_R = 12.5 min) to afford compound **3** (7.4 mg). Fr. III (42.0 g) was isolated by Sephadex LH-20 gel CC (eluted with 10%, 30%, 60%, 90%, and 100% MeOH/H_2O) to yield subfractions III-1–III-2. Compound **2** (10.0 mg) was purified from Fr. III-2 (17.0 g) by repeatedly ODS (MeOH–H_2O, gradient 10% → 100%), silica gel CC (chloroform/MeOH/H_2O, gradient 20:1:0.1 → 5:5:0.5) and semi-preparative HPLC (22% CH_3CN, 3 mL/min, t_R = 24.5 min).

3.3.1. Bodinioside E (*1*)

White amorphous powder; $[\alpha]_D^{19.3}$ −29.05 (c 0.19, MeOH); IR (KBr) υ_{max} 3428, 1734, 1701, 1636 cm^{-1}; ^{1}H- and ^{13}C NMR data, see



1

3

Fig. 2. Key HMBC correlations for compounds **1** and **3**.

Tables 1 and 2; ESI-MS (pos.) *m/z* 867 ($[M+Na]^+$); HRESIMS (pos.) *m/z* 867.4117 ($[M+Na]^+$) (calcd for $C_{42}H_{68}O_{17}Na$, 867.4143).

3.3.2. Bodinioside F (**2**)

White amorphous powder; $[\alpha]_D^{19.3}$ −88.97 (c 0.09, MeOH + $CHCl_3$ 2:1); ^1H- and ^{13}C NMR data, see Tables 1 and 2; ESI-MS (neg.) *m/z* 811 ($[M–H_2O–H]^-$); HRESIMS (neg.) *m/z* 811.4470 ($[M–H_2O–H]^-$) (calcd for $C_{42}H_{67}O_{15}$, 811.4480).

3.3.3. Bodinioside G (**3**)

White amorphous powder; $[\alpha]_D^{19.3}$ −45.71 (c 0.32, MeOH); ^1H-NMR and ^{13}C NMR data, see Tables 1 and 2; ESI-MS (neg.) *m/z* 827 ($[M–H_2O–H]^-$); HRESIMS (neg.) *m/z* 827.4424 ($[M–H_2O–H]^-$) (calcd for $C_{42}H_{67}O_{16}$, 827.4423).

3.4. Acid hydrolysis and GC analysis of compounds **1–3** (Zhao et al., 2007)

Compounds **1–3** (each 5.0 mg) were hydrolyzed with 9% HCl at 90 °C for 5 h. The reaction liquid was filtered after being cooled to 2–4 °C, and the filtered liquor was freeze-dried to obtain dry residual. The dried material was dissolved in dry pyridine (100 μL), then 0.1 M L-cysteine methyl ester hydrochloride (200 μL) was added, and the mixture was heated at 60 °C for 1 h. Then 150 μL of HMDS–TMCS (hexamethyldisilazane–trimethylchlorosilane, 2:1) was added, and the mixture was heated at 60 °C for another 30 min. After centrifugation, the supernatant was subjected to GC analysis under the following conditions: column temp 150–280 °C at 5°/min, carrier gas N_2 (1 mL/min), injector temp 230 °C and detector temp 250 °C, split ratio 1:10. The standards were prepared following the same procedure. Under these conditions, the retention time of D-glucoside derivative was 22.03 min. During co-injection studies, identical retention times were observed between the different hydrolysates and authentic standards.

Competing financial interest

The authors declare no competing financial interest. Q7

Supplementary data

1D and 2D NMR, IR, EIMS, HREIMS data of compounds **1–3** are available free of charge via the internet.

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