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Note

Two new complex triterpenoid saponins from *Gledistsia dolavayi* Franch.

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Two new triterpenoid saponins, gledistside A (1) and gledistside B (2), isolated from the fruits of *Gledistsia dolavayi* Franch., were characterized as the 3,28-*O*-bisdesmoside of echinocystic acid acylated with monoterpene carboxylic acids. On the basis of spectroscopic and chemical evidence, their structures were elucidated as 3-*O*-β-D-xylopyranosyl-(1→2)-α-L-arabinopyranosyl-(1→6)-β-D-glucopyranosyl-28-*O*-β-D-xylopyranosyl-(1→3)-β-D-xylopyranosyl-(1→4)-[β-D-galactopyranosyl-(1→2)]-α-L-rhamnopyranosyl-(1→2)-{6-*O*-[2,6-dimethyl-6(*S*)-hydroxy-2-*trans*-2,7-octadienoyl]}-β-D-glucopyranosylechinocystic acid (1) and 3-*O*-β-D-xylopyranosyl-(1→2)-α-L-arabinopyranosyl-(1→6)-β-D-glucopyranosyl-28-*O*-β-D-xylopyranosyl-(1→3)-β-D-xylopyranosyl-(1→4)-[β-D-galactopyranosyl-(1→2)]-α-L-rhamnopyranosyl-(1→2)-{6-*O*-[2-hydroxymethyl-6-methyl-6(*S*)-hydroxy-2-*trans*-2,7-octadienoyl]}-β-D-glucopyranosylechinocystic acid (2). The complete ¹H and ¹³C assignments of saponins 1 and 2 were achieved on the basis of 2D NMR spectra including HMQC-TOCSY, TOCSY, ¹H–¹H COSY, HMBC, ROESY and HMQC spectra. Copyright © 2002 John Wiley & Sons, Ltd.

INTRODUCTION

Gledistsia dolavayi Franch. (*Leguminosae*) is mainly distributed in Guizhou, Yunnan province, China, and has been used as a substitute for soap in some areas because its water extracts are abundant in saponins.[1] We have reported one new natural product, GS-C′, from the n-butanol fraction of water extracts of *Gledistsia dolavayi* Franch.[2] Further studies led to the isolation of two new complex saponins, gledistside A and B (**1** and **2**) (Fig. 1) that were characterized as the 3,28-*O*-bisdesmoside of echinocystic acid acylated with monoterpene carboxylic acids. This paper discusses the structure elucidation of these new saponins on the basis of spectroscopic and chemical evidence.

RESULTS AND DISCUSSION

Identification of the aglycone of saponins **1** and **2** was carried out by direct comparison of the ¹³C NMR data with similar structures reported in the literature.[2–5] The ¹³C NMR

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chemical shifts of the triterpene parts of **1** and **2** closely resemble those of the aglycone of echinocystic acid 3-*O*-β-D-glucopyranoside. Therefore, the aglycone of saponins **1** and **2** was determined to be echinocystic acid. The ¹H signal assignments of the aglycone were achieved from an HMQC spectrum. Finally, the ¹H and ¹³C signal assignments were confirmed by the data from ¹H–¹H COSY, TOCSY, HMQC-TOCSY, HMBC and ROESY spectra. These results are summarized in Table 1.

Individual sugar residues are indicated by capital letters (A–G and I, see Fig. 1) in the structures of **1** and **2**. ¹³C resonances are identified by a capital letter and the number of the ring carbon atom (e.g. A₂) and ¹H resonances are identified by the capital letter H in addition to a capital letter and the number of the ring proton atom (e.g. H-A₂).
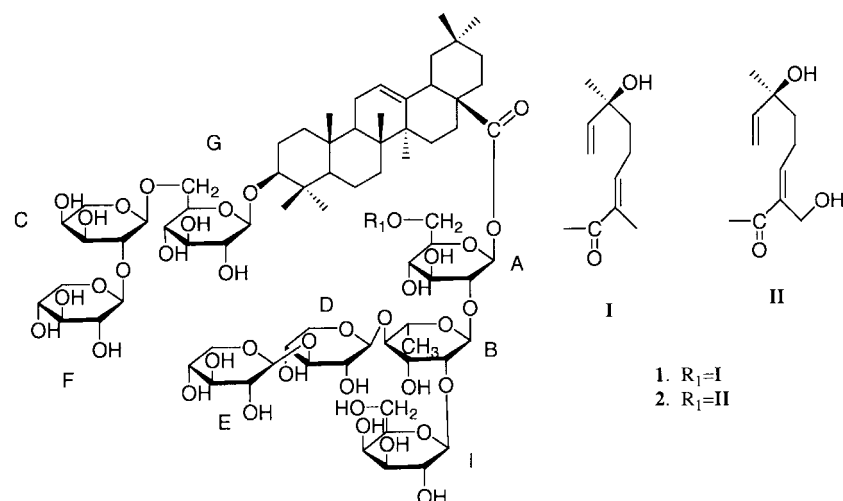
Saponin **1** was obtained as a white powder, m.p. 184–186 °C, $[\alpha]_D^{26} - 23.04°$ (*c* 0.36, MeOH). Negative ion high-resolution fast atom bombardment mass spectrometry (HR-FABMS) showed a quasi-molecular ion peak at *m/z* 1797.8420 [M − H]⁻ and established the molecular formula as $C_{84}H_{134}O_{41}$ (calcd for $C_{84}H_{133}O_{41}$ 1797.8322). The result was further confirmed by ¹³C (DEPT) spectra and FABMS showing a molecular ion peak at *m/z* 1798 (M⁻).

The ¹³C spectrum of **1** suggested the presence of three moieties: triterpene (the aglycone), sugar residue and monoterpene (Table 2) moiety. The structure of the

Figure 1. Structures of saponins **1** and **2**.

Table 1. ^{1}H and ^{13}C NMR data for the aglycone of saponins **1** and **2** (δ in C$_5$D$_5$N; J in Hz)

	1		**2**	
Atom	δ_C	δ_H	δ_C	δ_H
1	39.1	1.65; 1.16	39.2	1.64; 1.15
2	26.9	2.28; 1.88	27.0	2.28; 1.88
3	88.9	3.47 (brd, 9.23)	89.0	3.47 (dd, 3.44, 9.23)
4	39.7		39.7	
5	56.2	0.89	56.2	0.89
6	18.8	1.75; 1.54	18.9	1.75; 1.53
7	33.7	1.62; 1.32	33.7	1.64; 1.37
8	40.2		40.3	
9	47.3	1.85	47.4	1.85
10	37.2		37.3	
11	24.0	2.19; 2.04	24.1	2.19; 2.05
12	122.8	5.61 (brs)	122.9	5.63 (brs)
13	144.4		144.5	
14	42.3		42.3	
15	36.1	2.22; 1.96	36.1	2.22; 1.97
16	74.2	5.19 (brs)	74.2	5.20 (brs)
17	49.4		49.5	
18	41.6	3.39 (brd, 13.78)	41.6	3.40 (dd, 3.67, 13.78)
19	47.5	2.71 (brt, 13.17); 1.31	47.5	2.70; 1.31
20	30.9		30.9	
21	36.3	2.37; 1.25	36.3	2.38; 1.25
22	32.1	2.33; 2.15	32.1	2.34; 2.14
23	28.4	1.30 (s)	28.5	1.30 (s)
24	17.2	0.98 (s)	17.3	0.95 (s)
25	16.0	0.91 (s)	16.0	0.92 (s)
26	17.7	1.08 (s)	17.7	1.10 (s)
27	27.3	1.84 (s)	27.3	1.84 (s)
28	176.0		176.1	
29	33.3	0.91 (s)	33.3	0.91 (s)
30	24.8	1.06 (s)	24.9	1.05 (s)

monoterpene moiety in **1** was determined as structure **I** by comparison of its ^{13}C NMR chemical shifts with those reported in the literature.[6,7] The structure of **I** was further confirmed by 2D NMR spectra such as TOCSY, ^{1}H–^{1}H

COSY, HMQC-COSY, HMQC-TOCSY and HMBC spectra. The ^{13}C NMR spectrum of **1** showed eight anomeric carbon signals at δ 107.7 (I$_1$), 106.9 (G$_1$), 106.3 (F$_1$), 106.1 (E$_1$), 106.0 (D$_1$), 102.4 (C$_1$), 100.6 (B$_1$) and 94.5 (A$_1$). The ^{13}C

Table 2. ^{1}H and ^{13}C NMR data for the monoterpene of saponins **1** and **2** (δ in C$_5$D$_5$N; J in Hz)

Atom	**1** δ_C	**1** δ_H	**2** δ_C	**2** δ_H
1′	168.2		167.9	
2′	127.8		133.1	
3′	143.6	7.03 (t, 7.11)	146.9	7.21 (t, 7.83)
4′	24.1	2.46; 2.33	24.2	2.69; 2.60
5′	41.6	1.71	42.0	1.80; 1.74
6′	72.3		72.4	
7′	146.7	6.12 (dd, 10.90, 17.26)	146.6	6.09 (dd, 11.00, 17.41)
8′	111.9	5.56 (brd, 17.26)	112.0	5.53 (dd, 1.37, 17.41)
		5.17 (brd, 10.90)		5.15 (dd, 1.37, 11.00)
9′	12.6	1.85 (s)	56.4	4.72 (s)
10′	28.6	1.46 (s)	28.7	1.45 (s)

signals of each sugar residue were assigned mainly using an HMQC-TOCSY spectrum (Table 3).[8–12] Compared with GS-C′,[2] saponin **1** had the same seven sugar residues except for residue **I**. The ^{13}C NMR chemical shifts of residue **I** were at δ 107.7, 77.3, 75.5, 73.4, 70.3 and 62.4 and are characteristic of β-D-galactopyranosyl.[13] Residue **I** was determined to be β-D-galactopyranosyl on the basis of the following evidence: (1) FABMS showed a ion peak at m/z 1636 [M − 1 − 162]$^-$, suggesting that the terminal residue was a 6-oxygated hexose rather than a 6-deoxy hexose or pentose; (2) The TOCSY spectrum (t_m = 60 ms) showed correlation peaks from protons H-I$_1$ (anomeric) to H-I$_4$, which is characteristic of a *galacto* configuration and could be distinguished from *gluco* and *manno* configurations;[9,14,15] furthermore, the HMQC-TOCSY spectrum (t_m = 150 ms) showed correlation peaks from carbons I$_1$ (anomeric) to I$_4$ with H-I$_1$ (anomeric) and also confirmed that residue **I** had a *galacto* configuration;[8–12] (3) its ^1J(H-1,C-1) coupling constant of 154 Hz was smaller than 165 Hz, which is diagnostic of a β-configuration.[14–16] The presence of galactose was further confirmed by GC-MS.

Carbon A$_6$ shifted downfield to δ 64.4 (normally at δ 62 for β-D-glucopyranosyl), suggested that A$_6$ was esterified by a monoterpenyl moiety. Compared with GS-C′,[2] B$_2$ shifted down field from δ 71.8 to δ 81.4, suggesting that residue **I** is connected to B$_2$. These assignments were further confirmed by the HMBC spectrum, which showed long-range correlations between H-A$_{6a}$ (δ 4.90, brd, 12.11 Hz), H-A$_{6b}$ (δ 4.74, dd, 12.11 Hz, 4.39 Hz) and C-1′ (δ 168.2) of monoterpenyl **I**, H-I$_1$ (δ 5.13) and B$_2$ (δ 81.4). Other linkage sites between sugar residues and between the oligosaccharide segment and the aglycone were also confirmed by the HMBC spectrum. The long-range correlations between H-G$_1$ (δ 4.88) and C-3 (δ 88.9) of the aglycone, H-C$_1$ (δ 5.13) and G$_6$ (δ 69.8) in addition to H-F$_1$ (δ 4.96, d, 6.36 Hz) and C$_2$ (δ 80.6) suggested a trisaccharide segment connected to C-3 of the aglycone. The correlations between H-E$_1$ (δ 5.10, d, 7.72 Hz) and D$_3$ (δ 87.4), H-D$_1$ (δ 5.14) and B$_4$ (δ 83.2), H-B$_1$ (δ 6.45, brs) and A$_2$ (δ 77.2), H-A$_1$ (δ 6.07, brs) and C-28 (δ 176.0) of the aglycone ascertained that the oligosaccharide segment was connected to C-28 of the aglycone. Hence the structure of **1** was determined

to be 3-O-β-D-xylopyranosyl-(1→2)-α-L-arabinopyranosyl-(1→6)-β-D-glucopyranosyl-28-O-β-D-xylopyranosyl-(1→3)-β-D-xylopyranosyl-(1→4)-[β-D-galactopyranosyl-(1→2)]-α-L-rhamnopyranosyl-(1→2)-6-O-[2,6-dimethyl-{6(S)-hydroxy-2-*trans*-2,7-octadienoyl]}-β-D-glucopyranosylechinocystic acid and named gledistside A (**1**) (Fig. 1).

Saponin **2** was obtained as a white powder. m.p. 195–197 °C, [α]$_D^{26}$ − 40.68^0 (c 0.26, MeOH). Its HR-FABMS spectrum established the molecular formula as C$_{84}$H$_{134}$O$_{42}$ (found m/z 1814.8337 (M$^-$), calcd 1814.8401). The ^{13}C NMR chemical shifts of **2** were similar to those for **1** except for the monoterpenyl moiety. The structure of the monoterpenyl moiety in **2** was determined as structure **II** by comparison of the ^{13}C NMR data with those reported in the literature,[6,7] which was further confirmed by the 2D NMR spectra. Similarly to **1**, carbon A$_6$ shifted downfield to δ 64.5 and B$_2$ shifted downfield from δ 71.8 to δ 81.4 in comparison with GS-C′.[2] These findings suggested that A$_6$ was esterified by monoterpenyl **II** and residue **I** was connected to B$_2$, which was further confirmed by the HMBC spectrum, showing long-range correlations between H-A$_{6a}$ (δ 4.90, brd, 12.10 Hz), H-A$_{6b}$ (δ 4.75) and C-1′ (δ 167.9) of monoterpene **II**, H-I$_1$ (δ 5.13) and B$_2$ (δ 81.4). Therefore, the structure of **2** was determined to be 3-O-β-D-xylopyranosyl-(1→2)-α-L-arabinopyranosyl-(1→6)-β-D-glucopyranosyl-28-O-β-D-xylopyranosyl-(1→3)-β-D-xylopyranosyl-(1→4)-[β-D-galactopyranosyl-(1→2)]-α-L-rhamnopyranosyl-(1→2)-{6-O-[2-hydroxymethyl-6-methyl-6(S)-hydroxy-2-*trans*-2,7-octadienoyl]}-β-D-glucopyranosylechinocystic acid and named gledistside B (**2**) (Fig. 1).

EXPERIMENTAL

General experimental procedures

Melting-points was measured on a Koffler melting-point apparatus produced at Sichuan University, China, and uncorrected. Optional rotations were measured on Horiba SEPA-300 digital polarimeter. IR spectra were measured using a Bio-Rad FTS-135 spectrometer. FABMS and HR-FABMS were performed on a VG Auto Spec-3000 spectrometer. Gas chromatography–mass spectrometry (GC–MS) experiments were carried out on an MD 800 instrument.

Table 3. ^{1}H and ^{13}C NMR data for sugar residues of saponins **1** and **2** (δ in C_5D_5N; J in Hz)

Atom	1 δ_C	1 δ_H	2 δ_C	2 δ_H
3-*O*-G-1	106.9	4.88	106.9	4.89
2	75.8	4.03	75.8	4.05
3	78.5	4.12	78.5	4.12
4	72.3^f	4.12	72.3^j	4.16
5	76.2	4.00	76.2	4.02
6	69.8	4.63 (brd, 9.08); 4.18	69.8	4.67 (brd, 9.08); 4.18
C-1	102.4	5.13	102.4	5.12
2	80.6	4.50	80.6	4.49
3	72.7	4.39	72.7	4.39
4	67.6	4.30	67.6	4.31
5	64.4^g	4.28; 3.74 (brd, 10.90)	64.5^k	4.29; 3.74 (brd, 9.90)
F-1	106.3	4.96 (d, 6.36)	106.4	4.96 (d, 6.85)
2	75.3	4.00	75.3	4.02
3	78.0	4.06	78.0	4.13
4	70.9^h	4.11	71.0^l	4.13
5	67.4^l	4.38; 3.57 (dd, 12.41, 9.63)	67.4^m	4.38; 3.57 (dd, 12.35, 8.44)
28-*O*-A-1	94.5	6.07 (d, 8.17)	94.6	6.05 (d, 7.95)
2	77.2	4.25	77.2	4.25
3	78.9	4.17	78.9	4.16
4	71.5	4.05	71.6	4.05
5	76.2	4.09	76.2	4.09
6	64.4^g	4.90 (brd, 12.11); 4.74 (dd, 12.11, 4.39)	64.5^k	4.90 (brd, 12.10); 4.75
B-1	100.6	6.45 (brs)	100.6	6.46 (brs)
2	81.4	4.85 (brs)	81.4	4.84 (brs)
3	72.3^f	4.65 (brd, 9.39)	72.3^j	4.67 (brd, 8.80)
4	83.2	4.25	83.2	4.26
5	68.3	4.35	68.4	4.35
6	18.7	1.62 (d, 4.54)	18.7	1.62 (d, 4.77)
D-1	106.0	5.14	106.0	5.14
2	75.0	3.99	75.0	3.98
3	87.4	3.90	87.5	3.92
4	69.2	3.95	69.2	3.96
5	66.8	4.08; 3.34 (dd, 12.87, 7.42)	66.8	4.08; 3.34 (dd, 12.10, 7.34)
E-1	106.1	5.10 (d, 7.72)	106.1	5.09 (d, 7.46)
2	75.2	4.00	75.2	3.99
3	78.1	4.14	78.2	4.12
4	70.9^h	4.11	71.0^l	4.12
5	67.4^i	4.26; 3.64 (dd, 10.90, 6.81)	67.4^m	4.26; 3.64 (dd, 11.25, 7.46)
I-1	107.7	5.13	107.7	5.13
2	73.4	4.50	73.4	4.51
3	75.5	4.05	75.5	4.06
4	70.3	4.47 (brs)	70.3	4.47 (brs)
5	77.3	3.94	77.3	3.95
6	62.4	4.33	62.4	4.33

$^{a-m}$ Signals overlap with each other.

All NMR experiments were recorded on a Bruker DRX-500MHz spectrometer at room temperature. Compounds **1** (57 mg) and **2** (62 mg) were dissolved in about 0.4 ml of C_5D_5N. ^{1}H and ^{13}C chemical shifts were calibrated with the lowest field signal of C_5D_5N (δ 8.71 and δ 149.9). ^{1}H and ^{13}C NMR spectra were acquired under standard conditions. The NMR conditions for all compounds were as follows: 1D spectra were acquired using 64K data points for ^{1}H and ^{13}C spectra. 32K data points were used for the processing with no window function for ^{1}H and exponential function (LB = 4) for ^{13}C.

Standard pulse sequences were used for 2D spectra. Z-PFG was used to obtain HMQC, HMBC and DQF H–H COSY spectra. Relaxation delays of 1.5 or 2 s were used for

all 2D NMR experiments. 2D spectra used 1024×256 (H–H COSY, HMQC, ROESY and HMQC-TOCSY) and 2048×256 (HMBC) data point matrices, then zero filled to 1024×512 and 2048×512, respectively. A non-shifted sine window function was used along both F_1 and F_2 axes for H–H COSY, HMQC, HMBC and a $90°$ shifted sine window function was used along the F_1 and F_2 axes for TOCSY and ROESY. TOCSY experiment used a 60 ms mixing time. HMBC utilized 62.5 ms [optimized to ^nJ(C,H) $= 8$ Hz, $n > 1$] as the delay time to achieve ^{1}H–^{13}C long range correlations. A spin-lock of 350 ms (for **1** and **2**) was used in ROESY experiments. The HMQC–TOCSY experiment utilized a spin-lock of 180 ms as the mixing time. Data processing was carried out on an HP VL600 computer with Bruker XWINNMR programs (Version 2.7).

Plant material

The fruits of *Gledistsia dolavayi* Franch. were collected in Yuanjiang county of Yunnan province in September 1997. A voucher specimen is deposited in the Herbarium of Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and isolation

The crushed and dried fruits (2 kg) were extracted with 50% hot EtOH three times to afford an EtOH extract. The extract was suspended in water, then partitioned successively with chloroform and n-butanol. The n-butanol fraction (17.5 g) was subjected to silica gel column chromatography with $CHCl_3$–MeOH–H_2O (7:3:0.5) as eluent, then to RP-8 column chromatography with MeOH–H_2O (7:3 or 6:4) as eluent to afford saponins **1** (124 mg) and **2** (95 mg).

Acid hydrolysis and GC–MS analysis

A solution of **1** (8 mg) in 2 M HCl–dioxane (1:1) (1 ml) was heated at $95°$C for about 6 h and the reaction mixture was blowed to dryness with a stream of nitrogen. The residue was dissolved in pyridine (0.5 ml), then $(CH_3)_3SiNHSi(CH_3)_3$ (0.5 ml) was added. After 10 min at room temperature, the reaction mixture was blown to dryness with a stream of nitrogen. The residue was dissolved in diethyl ether then directly subjected to GC–MS analysis.

GC–MS experiments were carried out on an MD 800 instrument. Trimethylsilyl ether derivatives were separated using an HP Ac-5 capillary column (0.25×30m). Nitrogen was used as the carrier gas. The initial column oven temperature was $180°$C, then increased at $5°$C min^{-1} to a final value of $240°$C. The sugars were determined by comparison of retention times (t_R) and MS behaviour with standard sugars: t_R (min) Glc 6.85 (m/z 482), Ara 4.19 (m/z 438), Xyl 5.06 (m/z 438), Rha 4.30 (m/z 452), Gal 6.50 (m/z 482).

Spectral data

Gledistside A (**1**): white powder, m.p. 184–186 °C. $[\alpha]_D^{26}$ − 23.04° (c 0.36, MeOH). HR-FABMS: m/z 1797.8420 [M − H]$^-$ (calcd for $C_{84}H_{133}O_{41}$ 1797.8322). FABMS: m/z 1798 (M$^-$), 1666 [M − 132]$^-$, 1636 [M − 162]$^-$, 1534 [M − 132 − 132]$^-$, 1372 [M − 132 − 132 − 162]$^-$, 898 [470 (aglycone) + 164 + 132 + 132]$^-$, 765 [470 (aglycone)-1 + 164 + 132]$^-$, 631 [470 (aglycone)-1 + 162]$^-$, 469 [470 (aglycone)-1]$^-$, 337, 263. IR (KBr): v_{max} 3413, 2930, 1736, 1707, 1645, 1452, 1375, 1307, 1163, 1081, 1045, 824, 786 cm^{-1}. For ^{1}H and ^{13}C data, see Tables 1–3.

Gledistside B (**2**): white powder, m.p. 195–197 °C. $[\alpha]_D^{26}$ − 40.68° (c 0.26, MeOH). HR-FABMS: m/z 1814.8337 (M$^-$) (calcd for $C_{84}H_{134}O_{42}$ 1814.8350). FABMS: m/z 1814 (M$^-$), 1682 [M − 132]$^-$, 1652 [M − 162]$^-$, 1550 [M − 132 − 132]$^-$, 1368 [M − 132 − 132 − 132]$^-$, 1220 [M − 132 − 132 − 132 − 162]$^-$, 897 [470 (aglycone) − 1 + 164 + 132 + 132]$^-$, 766 [470 (aglycone) + 164 + 132]$^-$, 631 [470 (aglycone) − 1 + 162]$^-$, 468 [470 (aglycone)-2]$^-$, 339, 263. IR (KBr): v_{max} 3403, 2931, 1737, 1702, 1645, 1452, 1374, 1307, 1163, 1079, 1046, 820, 786 cm^{-1}. For ^{1}H and ^{13}C data, see Tables 1–3.

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