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Two new triterpene saponins from *Lysimachia davurica*

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Two new saponins, named davuricoside L (**1**) and davuricoside O (**2**), have been isolated from the whole plants of *Lysimachia davurica*. Their structures were determined by 1D and 2D NMR, FAB-MS techniques, and chemical methods.

Keywords: *Lysimachia davurica*; Primulaceae; Triterpene saponin; Davuricosides L and O

1. Introduction

Lysimachia davurica Ledeb. (Primulaceae) is a folklore medicinal plant that grows in northeastern China. The whole plant is used to treat hypertension [1]. However, no phytochemical study has been reported yet. During our ongoing screening for active constituents on hypertension and blood circulation promotion, we have isolated some organic acids and flavones from this plant [2,3]. We now report the isolation and structural elucidation of two new saponins, davuricoside L (**1**) and davuricoside O (**2**).

2. Results and discussion

Saponin **1** was obtained as an amorphous white powder, mp 243–246°C, $[\alpha]_D^{20} +19.51$ (*c* 0.63, MeOH), and gave a positive result for the Liebermann–Burchard test. Its HR-FABMS showed a quasi-molecular ion peak at *m/z* 1115.5629 ($[M + Na]^+$), corresponding to a formula of $C_{53}H_{88}O_{23}Na$ (calcd 1115.5638). The six tertiary methyl groups (δ 1.75, 1.24, 1.15, 1.02, 0.94 and 0.88) and one trisubstituted olefinic proton (δ 5.50, br t) observed in the 1H NMR spectrum, as well as the information from the ^{13}C NMR spectrum (six sp^3 carbons at δ 15.8, 16.8, 17.2, 27.4, 28.2 and 28.4, two sp^2 olefinic carbons at δ 122.6 and 144.7),

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Table 1. ^{13}C NMR spectral data for the aglycone moieties of **1** and **2** (125 MHz in pyridine- d_6).

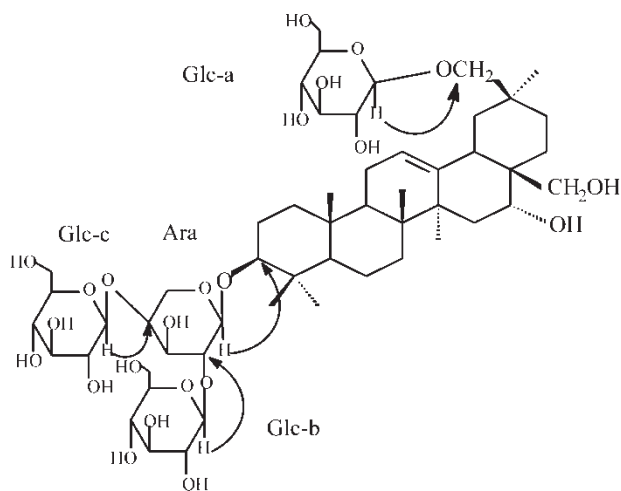
Carbon	1	2
1	39.0	38.9
2	26.4	26.6
3	88.9	89.1
4	39.5	39.5
5	55.9	55.7
6	18.5	18.4
7	33.3	33.2
8	40.1	39.9
9	47.2	47.0
10	36.9	36.7
11	23.8	23.0
12	122.6	122.7
13	144.7	144.6
14	41.1	41.0
15	34.8	34.7
16	74.1	74.0
17	42.0	41.8
18	41.5	41.5
19	43.3	43.5
20	35.5	35.5
21	32.3	32.1
22	28.4	28.7
23	28.4	28.1
24	16.8	16.7
25	15.8	15.7
26	17.2	17.0
27	27.4	28.4
28	69.3	69.3
29	28.2	27.3
30	75.2	75.2

showed that the compound was a triterpene saponin. Arabinose (Ara) and glucose were detected after acid hydrolysis. Assignment for all carbon signals was achieved by 2D NMR (table 1); the ^{13}C NMR data was compared with that of pridentigenin E (3 β ,16 α ,28,30-tetrahydroxy-olean-12-ene) [4]. Both compounds showed very similar ^{13}C NMR data except C-3 and C-30, the former displaying signals down-shifted 11 and 8 ppm respectively, which suggest that the aglycone of **1** is pridentigenin E and the glycoside linkages are at its C-3 and C-30. Saponin **1** was a bisdesmoside glycoside.

The HMQC spectrum of saponin **1** showed that it contained four sugar units, their anomeric protons at δ 4.89 (1H, d, $J = 8.0$ Hz), 4.91 (1H, d, $J = 5.0$ Hz), 5.11 (1H, d, $J = 7.5$ Hz) and 5.14 (1H, d, $J = 8.0$ Hz) correlated with carbons signals at δ 104.3, 105.4, 105.5 and 105.7 respectively. The spin-systems associated with four individual monosaccharides were identified by TOCSY experiment with the aid of a ^1H - ^1H COSY spectrum. All ^1H and ^{13}C signals of the sugar moieties were assigned by an HMQC experiment (table 2). Combined with spin-spin couplings, the four sugar units were identified as one α -arabinopyranoside (Ara) and three β -glucopyranosides (Glc). The sugar sequences of the oligosaccharide chains as well as the glycoside sites were subsequently determined by HMBC spectrum. In the HMBC spectrum of **1** (figure 1), correlations occurred between the anomeric proton of arabinose at δ 4.95 (1H, d, $J = 5.0$ Hz) and C-3 of aglycone at δ 88.9, the anomeric proton of glucose-b at δ 5.11 (1H, d, $J = 7.5$ Hz) and the C-2 of arabinose at δ 80.7, the anomeric proton of glucose-c at δ 5.14 (1H, d, $J = 8.0$ Hz) and the C-4 of arabinose at δ 77.0, the anomeric proton of glucose-a at δ 4.89 (1H, d, $J = 8.0$ Hz)

Table 2. ^1H and ^{13}C NMR spectral data for the sugar moieties of **1** and **2** (125 MHz for ^{13}C and 500 MHz for ^1H NMR in pyridine- d_6).

	1		2	
	^1H (J Hz)	^{13}C	^1H (J Hz)	^{13}C
<i>Sugar at C-3</i>				
1	4.95 (5.0)	104.3	4.95 (6.5)	105.1
2	4.52	80.7	4.32	82.8
3	4.42	72.3	4.38	77.1
4	4.47	77.0	4.22	73.3
5	3.80	63.5	4.25	77.8
6				174.0
<i>Sugar at C-2 of inner sugar</i>				
1	5.11 (7.5)	105.5	5.36 (7.0)	105.6
2	4.06	76.1	4.17	76.6
3	3.86	78.6	4.38	77.7
4	4.22	72.0	4.23	71.8
5	3.95	78.3	3.99	78.4
6	4.51, 4.37	63.2	4.50, 4.36	62.6
<i>Sugar at C-4 of inner sugar</i>				
1	5.14 (8.0)	105.4		
2	4.07	75.7		
3	3.95	78.6		
4	4.26	71.8		
5	3.86	78.2		
6	4.52, 4.37	62.7		
<i>Sugar at C-30</i>				
1	4.89 (8.0)	105.7	4.90 (8.0)	106.0
2	4.39	75.2	4.56	75.3
3	4.13	78.3	4.22	78.5
4	4.23	71.5	4.32	71.5
5	3.95	77.9	3.92	78.2
6	4.57, 4.39	62.7	4.58, 4.44	62.9

Figure 1. Structure and key HMBC correlations of saponin **1**.

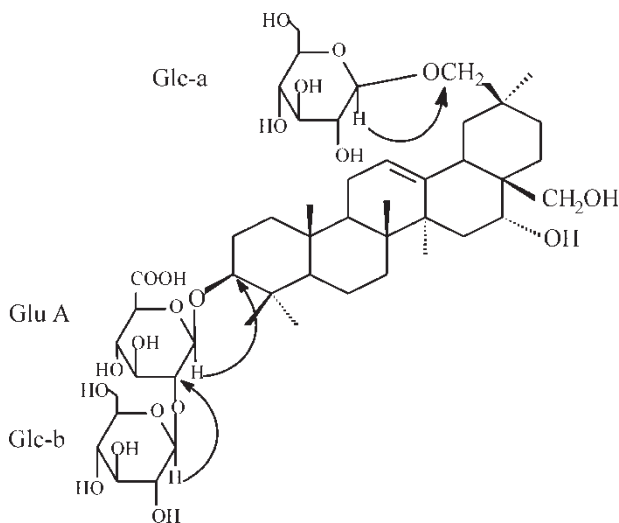


Figure 2. Structure and key HMBC correlations of saponin **2**.

and C-30 of the aglycone at δ 75.2, suggesting the sugar sequences of the oligosaccharide chains shown in figure 1.

Thus, the structure of the saponin **1** was established as 3-*O*- β -D-glucopyranosyl-(1 \rightarrow 2)-[β -D-glucopyranosyl-(1 \rightarrow 4)]- α -L-arabinopyranosyl pridentigenin E 30-*O*- β -D-glucopyranoside, named davuricoside L.

Saponin **2** was obtained as an amorphous white powder, mp 238–240°C, $[\alpha]_D^{20} + 8.11$ (*c* 0.50, MeOH), and gave a positive result to the Liebermann–Burchard test. Its HR-FABMS showed a quasi-molecular ion peak at m/z 1013.5342 ($[M + K]^+$), corresponding to a formula of $C_{48}H_{78}O_{20}K$ (calcd 1013.5321). A comparison of the NMR spectra of **2** with those of **1** (table 2) showed that they share the same aglycone.

The 1H and the ^{13}C NMR resonances of the sugar moiety indicated the presence of one glucuronic acid (Glu A) and two glucose (Glc), and sugar anomeric protons at δ 4.90 (1H, d, $J = 8.0$ Hz), 4.95 (1H, d, $J = 6.5$ Hz), 5.36 (1H, d, $J = 7.0$ Hz) correlated with anomeric carbons at δ 105.1, 106.0, 105.63 respectively. Glucuronic acid and glucose were detected by acid hydrolysis of **2** using high-performance thin-layer chromatography (HPTLC). Each monosaccharide was deduced to be in a β -D-configuration from the coupling constant of the anomeric proton.

The sugar sequence and linkage positions of the saccharide chains were determined on the basis of HMBC. In the HMBC spectrum of **2**, the correlations between the anomeric proton of glucuronic acid at δ 4.95 (1H, d, $J = 6.5$ Hz) and C-3 of aglycone at δ 89.1, the anomeric proton of glucose-b at δ 5.36 (1H, d, $J = 7.0$ Hz) and the C-2 of glucuronic acid at δ 82.8, the anomeric proton of glucose-a at δ 4.90 (1H, d, $J = 8.0$ Hz) and C-30 of the aglycone at δ 75.2 suggest the sugar sequences of the oligosaccharide chains as shown in figure 2.

Therefore, the structure of saponin **2** was established as 3-*O*- β -D-glucopyranosyl-(1 \rightarrow 2)- β -D-glucuronopyranosyl pridentigenin E 30-*O*- β -D-glucopyranoside, named davuricoside O.

3. Experimental

3.1 General experiment procedures

Melting points were measured on a Fisher-Johns apparatus and are uncorrected. Optical rotations were obtained on a Perkin-Elmer 341 polarimeter. IR spectra were recorded on a Perkin-Elmer 983G spectrometer. NMR spectra were recorded on a Bruker AM-500 (500 MHz) instrument. FABMS were obtained on a Zabspec E spectrometer; ESIMS were obtained on an Esquire-LC00054 spectrometer. HPLC was performed using a Waters 510 pump with Alltech 500 ELSD (Evaporative Light Scattering Detector). For column chromatography, AB-8 resin (Tianjin Nankai), silica gel (200–300 mesh, Qingdao Haiyang) and ODS C₁₈ (35–50 μm, Alltech) were used. TLC and HPTLC (silica gel GF₂₅₄ precoated plates, Qingdao Haiyang) detection was obtained by spraying with 10% H₂SO₄ following heating.

3.2 Plant material

The *Lysimachia davurica* was collected in Jilin province, China, and identified by Dr Bao-Lin Guo, Institute of Medicinal Plants Development, Chinese Academy of Medical Sciences and Peking Union Medical College.

3.3 Extraction and isolation

The dried powdered plant (16 kg) was extracted with 95% EtOH and 50% EtOH twice under reflux respectively. The 95% EtOH and 50% EtOH extracts were then combined. After removal of the solvent by evaporation, the extracts were partitioned between H₂O and light petroleum (60–90°C), CHCl₃, EtOAc and n-BuOH, successively. The n-BuOH extract was chromatographed on an AB-8 resin column, eluting with H₂O and 30, 50, 70 and 95% EtOH. The 50% EtOH eluate was then chromatographed on a silica-gel column, eluting gradually with CHCl₃–MeOH (with 5% H₂O). The fraction containing **1** and **2** was subjected to ODS C₁₈ (35–50 μm) column and reverse-phase HPLC (MeOH–H₂O 41:59), to afford **1** (57 mg) and **2** (12 mg).

Saponin **1** is a white amorphous powder (MeOH–H₂O 9:1), mp 243–246°C, $[\alpha]_D^{20} +19.51$ (*c* 0.63, MeOH); IR (KBr) ν_{\max} (cm⁻¹): 3200 (OH), 2980, 2860, 1640, 1485, 1300, 1230, 1070, 940; ¹H NMR (C₅D₅N-d₅, 500 MHz) δ (ppm): 5.50 (1H, br t, H-12), 4.55 (1H, m, H-16), 4.44 (1H, d, *J* = 8.0 Hz, H-30a), 3.83 (1H, d, *J* = 8.0 Hz, H-30b), 3.64 (2H, s, H-28), 3.16 (1H, dd, *J* = 4.5, 12.0 Hz, H-3), 1.75 (3H, s, Me-27), 1.24 (3H, s, Me-29), 1.15 (3H, s, Me-23), 1.02 (3H, s, Me-24), 0.94 (3H, s, Me-26), 0.88 (3H, s, Me-25); ¹H NMR data of the saccharide residues, see table 2; ¹³C NMR (C₅D₅N-d₅, 125 MHz), see tables 1 and 2; FABMS *m/z* 1115 [M + Na]⁺, 1093 [M + H]⁺; HR-FABMS *m/z* 1115.5629, calcd for C₅₃H₈₈O₂₃Na.

Saponin **2** is a white amorphous powder (MeOH/H₂O 9:1), mp 238–240°C, $[\alpha]_D^{20} +8.11$ (*c* 0.50, MeOH); IR (KBr) ν_{\max} (cm⁻¹): 3420 (OH), 2970, 2870, 1720 (C = O), 1640, 1480, 1300, 1270, 1030, 950; ¹H NMR (C₅D₅N-d₅, 500 MHz) δ (ppm): 5.45 (1H, br t, H-12), 4.55 (1H, m, H-16), 4.35 (1H, d, *J* = 9.0 Hz, H-30a), 3.82 (1H, d, *J* = 9.0 Hz, H-30b), 3.63 (2H, s, H-28), 3.29 (1H, dd, *J* = 4.5, 11.5 Hz, H-3), 1.78 (3H, s, Me-27), 1.24 (3H, s, Me-29), 1.24

(3H, s, Me-23), 1.08 (3H, s, Me-24), 0.91 (3H, s, Me-26), 0.83 (3H, s, Me-25); ^1H NMR data of the saccharide residues, see table 2; ^{13}C NMR ($\text{C}_5\text{D}_5\text{N}-d_5$, 125 MHz), see tables 1 and 2; ESIMS m/z 1013 $[\text{M} + \text{K}]^+$, 997 $[\text{M} + \text{Na}]^+$, 974 $[\text{M} + \text{H}]^+$ HR-FABMS m/z 1013.5342, calcd for $\text{C}_{48}\text{H}_{78}\text{O}_{20}\text{K}$.

References

- [1] J.K. Tian, L.Z. Xu, Z.M. Zou, S.L. Yang. *Foreign Med. Sci. (fascicule Trad. Chin. Med.)*, **24**, 80–85 (2002).
- [2] J.K. Tian, Z.M. Zou, L.Z. Xu, S.L. Yang. *Chin. Trad. Herb Drugs*, **32**, 967–969 (2001).
- [3] J.K. Tian, Z.M. Zou, L.Z. Xu, S.L. Yang. *Chin. J. Chin. Mater. Med.*, **27**, 283–284 (2002).
- [4] Z.H. Jia, K. Koike, T. Ohmoto, M. Ni. *Phytochemistry*, **37**, 1389–1396 (1994).