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Two new triterpene saponins from *Lysimachia capillipes*

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Two new saponins, capilliposide G (**1**) and capilliposide H (**2**), were isolated from the whole plants of *Lysimachia capillipes.* Their structures were determined by 1D and 2D NMR, MS technique and chemical methods.

Keywords: *Lysimachia capillipes*; Triterpene saponin; Capilliposide G and H

1. Introduction

Lysimachia capillipes Hemsl (Primulaceae) is a folklore medicinal plant that grows in south-eastern China. The whole plant is used for treating cold and rheumatoid arthritis [1]. We have isolated some flavones from this plant [2]; now we continue to report the isolation and structural elucidation of two new saponins, capilliposide G (**1**) and capilliposide H (**2**).

2. Results and discussion

Compound **1** obtained as an amorphous white powder gave positive result to the Liebermann-Burchard test. The molecular formula was determined to be $C_{60}H_{96}O_{29}$ by HR-FAB-MS. In the negative ESIMS, it showed signal of quasi-molecular ions peak at *m/z* 1279 $[M - H]^-$. The seven tertiary methyl groups (δ 1.15, 1.02, 0.97, 0.92, 0.91, 0.80 and 0.70) and one methyl (δ 2.04) of acetate observed in the ^1H NMR spectrum, as well as information from the ^{13}C NMR spectrum (eight sp^3 carbons at δ 15.8, 16.2, 17.4, 19.1, 21.6, 25.0, 27.6 and 32.9) showed that the compound was a triterpene saponin. Glucose, xylose and arabinose were detected after acid hydrolysis. Four carbon signals connected with oxygen and two carbonyl signals of ester were observed in ^{13}C NMR of **1** besides signals of sugars; through HMBC,

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HMQC and $^{1}H-^{1}H$COSY analysis of **1**, the four carbons (δ 92.1, 88.7, 75.0 and 68.2) were assigned as C-13, C-3, C-22 and C-16. The carbonyl (δ 176.9) was assigned as C-28, while another carbonyl (δ 169.5) of an acetory was connected with C-16. Comparison of the ^{13}C NMR data with that of known leucolactone (28 → 13 lactone) [3] showed that the chemical shifts of C-28 and C-13 were accorded with that of leucolactone. In the NOESY spectrum of **1**, H-16 [6.03 (1H, d, J = 4.5 Hz)] was correlated to H-26 [0.92 (3H, s)], H-30 [0.80 (3H, s)] and H-22 [4.43 (1H, dd, J = 7.0, 6.0 Hz)], indicating that H-16 and H-22 were β configuration, The configuration of H-3 was to be α by the coupling pattern of H-3 [δ 3.06 (1H,dd, J = 4.5,11.5 Hz)]. The above analysis revealed that the aglycone of **1** was clarified to be 3β, 22α-dihydroxy-16α-acetoxy-28 → 13-lactone-oleanane.

The HMQC spectrum of compound **1** showed that it contained five sugar units; their anomeric protons at δ 5.55 (1H, d, J = 7.5 Hz), 5.40 (1H, d, J = 7.5 Hz), 4.87 (1H, d, J = 8.0 Hz), 4.81 (1H, d, J = 7.5 Hz) and 4.69 (1H, d, J = 5.5 Hz) were correlated with carbons signals at δ 103.9, 104.1, 104.2, 107.1 and 104.5 respectively. The spin-systems associated with disaccharide were identified by HSQC-TOCSY experiment with the aid of a $^{1}H-^{1}H$COSY spectrum. All ^{1}H and ^{13}C signals of the sugar moieties were assigned by HMQC experiment (tables 1 and 2). Combining with spin–spin couplings, the five sugar

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

C	*1*	*2*	*C*	*1*	*2*
1	38.6	38.6		α-L-Ara	α-L-Ara
2	26.1	26.0	1′	104.5	104.8
3	88.7	87.8	2′	79.1	80.5
4	39.3	38.7	3′	73.0	72.3
5	55.0	55.0	4′	78.6	79.7
6	18.1	18.1	5′	64.5	63.8
7	32.7	33.4		β-D-Glc I	β-D-Glc I
8	41.9	41.9	1″	104.1	103.6
9	49.3	49.4	2″	75.7	76.0
10	36.3	36.3	3″	77.1	77.9
11	30.8	30.8	4″	71.4	71.5
12	33.4	32.8	5″	78.0	78.4
13	92.1	91.8	6″	62.5	62.0
14	42.0	42.0		β-D-Glc II	β-D-Glc II
15	33.2	32.4	1‴	104.2	104.2
16	68.2	68.0	2‴	84.7	85.2
17	51.4	51.5	3‴	77.7	77.3
18	50.3	50.3	4‴	71.2	71.8
19	37.2	37.2	5‴	78.0	78.2
20	32.4	32.9	6‴	62.2	62.7
21	44.3	44.5		β-D-Xyl	β-D-Rha
22	75.0	74.7	1‴	107.1	102.0
23	27.6	27.7	2‴	75.2	72.3
24	16.2	16.3	3‴	77.5	71.1
25	15.8	15.9	4‴	70.2	73.9
26	17.4	17.4	5‴	67.0	69.7
27	19.1	19.0	6‴		18.5
28	176.9	176.6		β-D-Glc III	β-D-Glc III
29	32.9	32.9	1′′′′′	103.9	104.2
30	25.0	25.0	2′′′′′	75.4	75.9
Ac	169.5	169.1	3′′′′′	77.0	77.5
	21.6	21.6	4′′′′′	70.5	78.1
			5′′′′′	77.8	77.9
			6′′′′′	61.8	62.4

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

	1	***2***		***1***	***2***
H	δ_H (*J* in Hz)	δ_H (*J* in Hz)	H	δ_H (*J* in Hz)	δ_H (*J* in Hz)
	α-L-Ara	α-L-Ara		β-D-Xyl	α-L-Rha
1′	4.69(5.5)	4.77 (5.0)	1‴	4.81(7.5)	6.27(5.0)
2′	4.41	4.31	2‴	4.11	4.29
3′	4.33	4.39	3‴	4.19	3.88
4′	4.47	4.45	4‴	4.26	4.29
5′	3.85	3.90	5‴	3.70	3.86
5′	3.60	3.67	5‴	4.28	
	β-D-Glc I	β-D-Glc I	6‴		1.78(3H,d,6.0)
1″	5.40 (7.5)	5.63 (7.5)		β-D-Glc III	β-D-Glc III
2″	4.02	4.11	1′′′′′	5.55 (7.5)	5.62 (7.5)
3″	3.82	3.90	2′′′′′	4.54	4.40
4″	4.25	4.22	3′′′′′	3.95	3.93
5″	3.99	3.99	4′′′′′	4.13	4.26
6″	4.50	4.48	5′′′′′	3.97	3.89
6″	4.37	4.36	6′′′′′	4.49	4.56
	β-D-Glc II	β-D-Glc II	6′′′′′	4.34	4.46
1‴	4.87(8.0)	4.79(7.5)			
2‴	4.25	4.20			
3‴	3.76	3.85			
4‴	4.22	4.25			
5‴	4.03	4.12			
6‴	4.60	4.57			
6‴	4.48	4.35			

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units were identified as three β-D-glucopyranosides, one β-D-xylpyranoside and one α-D-arabinpyranoside.

The sugar sequences of the disaccharide chains as well as the glycoside sites were subsequently determined by HMBC spectrum. In the HMBC spectrum of **1** (figure 1), the correlations could be achieved between the anomeric proton of arabinose at δ 4.69 (1H, d, J = 5.5 Hz) and C-3 of aglycone at δ 88.7, the anomeric proton of glucose-I at δ 5.40 (1H, d, J = 7.5 Hz) and the C-2 of arabinose at δ 79.1, the anomeric proton of glucose-II at δ 4.87 (1H, d, J = 8.0 Hz) and the C-4 of arabinose at δ 78.6, the anomeric proton of xylose at δ 4.81

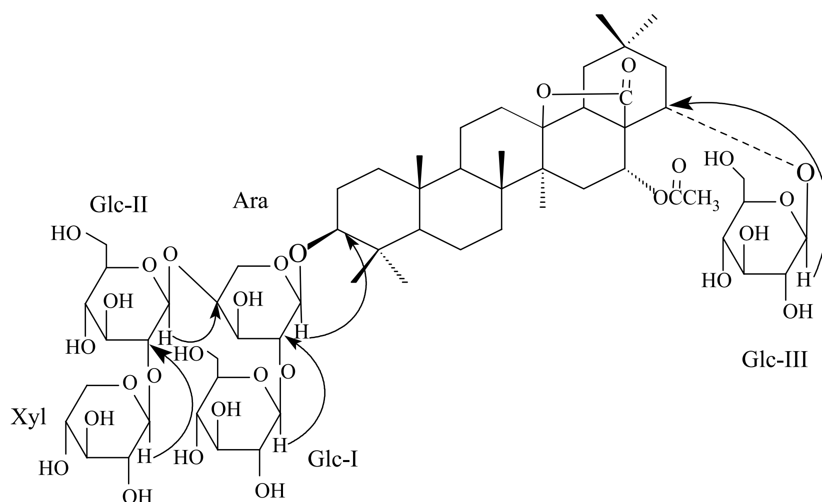

Figure 1. Structure and key HMBC correlations of **1**

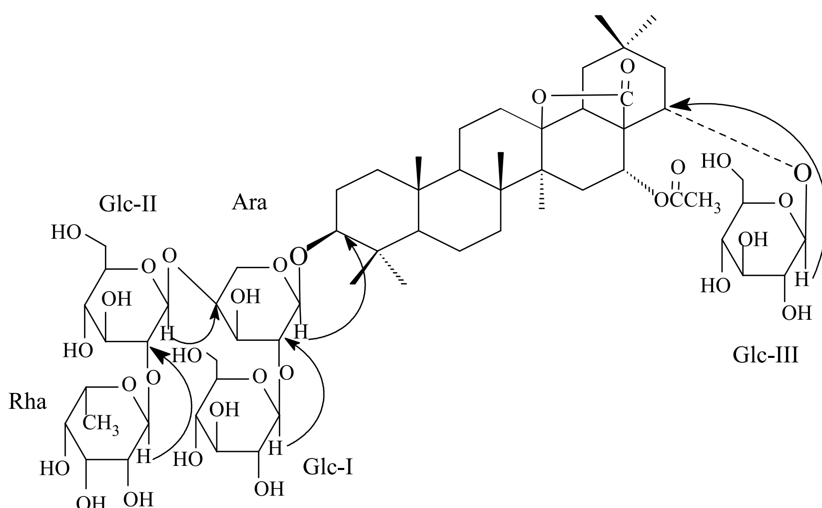

Figure 2. Structure and key HMBC correlations of **2**

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(1H, d, J = 7.5 Hz) and the C-2 of glucose-II at δ 84.7, the anomeric proton of glucose-III at δ 5.55 (1H, d, J = 7.5 Hz) and the C-22 of aglycone at δ 75.0 respectively, suggesting the sugar sequences of the disaccharide chains as shown in figure 1.

Thus, the structure of the **1** was established as 3β, 22α-dihydroxy-16α-acetoxy-28 → 13-lactone-oleanane-3-*O*-{β-D-xylpyranosyl-(1 → 2)-β-D-glucopyranosyl-(1 → 4)-[β-D-glucopyranosyl-(1 → 2)]-α-L-arabinpyranosyl}-22-*O*-β-D-glucopyranoside, named as capilliposide G.

The positive ESIMS of compound **2** showed a quasi-molecular ion peak at *m/z* 1317 $[M + Na]^+$ corresponding to a molecular formula $C_{61}H_{98}O_{29}$ confirmed by from HR-FAB-MS. Comparison of NMR spectrum of **2** with that of compound **1** showed very similar ^{13}C NMR data, except that the β-D-xylpyranoside in compound **1** was replaced by an α-L-rhamnopyranoside in compound **2**. Thus, **2** was identified as 3β, 22α-dihydroxy-16α-acetoxy-28 → 13-lactone-oleanane-3-*O*-{α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranosyl-(1 → 4)-[β-D-glucopyranos-yl-(1 → 2)]-α-L-arabinpyranoyl}-22-*O*-β-D-glucopyranoside, named as capilliposide H, figure 2.

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 measured on a Bruker AM-500 (500 MHz) instrument. FAB-MS data 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 Chemical Co.) and ODS C_{18} (35–50 μm, Alltech) were used. TLC and HPTLC (silica gel

GF_{254} precoated plates, Qingdao Haiyang Chemical Co.) detection was obtained by spraying 10% H_2SO_4 followed by heating.

3.2 Plant material

The *Lysimachia capillipes* was collected in Guizhou province, China, and identified by Dr Bao-Lin Guo, Institute of Medicinal Plants Development, Chinese Academy of Medical Sciences and Peking Union Medical College. The voucher specimen is deposited in Institute of Medicinal Plants Development, Chinese Academy of Medical Sciences and Peking Union Medical College.

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3.3 Extraction and isolation

The dried powdered plant materials (10 kg) were refluxed with 95% EtOH twice and then with 50% EtOH twice; the 95% EtOH extract and 50% EtOH extract were combined. After removal of the solvent by evaporation, the combined extracts were partitioned between H_2O and petroleum ether, $CHCl_3$, EtOAc and *n*-BuOH successively. The *n*-BuOH extract (1.5 kg) was chromatographed over AB-8 resin column, eluting with H_2O and 30, 50, 70 and 95% EtOH. 50% EtOH eluate (27 g) was chromatographed on Si gel column, eluting with $CHCl_3$–MeOH (MeOH contain 5% H_2O) from 90:10 to 40:60 in a gradient manner. Fraction 25 ($CHCl_3$–MeOH, 60:40; 1.3 g) was separated on ODS C_{18} (35–50 μm) column, using MeOH–H_2O (41.5:58.5) as eluent to afford **1** (43 mg) and **2** (17 mg).

3.3.1 Compound 1. white amorphous powder (MeOH–H_2O, 9:1), mp 229–231 °C, $[\alpha]_D^{20}$ − 5.00 (c 0.50, MeOH); IR (KBr)v_{max} cm^{-1} 3320 (OH), 2960, 2870, 1730, 1720, 1480, 1320, 1230, 1050, 950 cm^{-1}; ^1H NMR (C_5D_5N-d_5, 500 MHz) δ 6.03 (1H, d, $J = 4.5$ Hz, H-16), 4.43 (1H, dd, J = 6.0, 7.0 Hz, H-22), 3.06 (1H, dd, $J = 4.5$, 11.5 Hz, H-3), 2.04 (3H, s, acetate Me), 1.15 (3H, s, Me-27), 1.02 (3H, s, Me-23), 0.97 (3H, s, Me-24), 0.92 (3H, s, Me-26), 0.91 (3H, s, Me-29), 0.80 (3H, s, Me-30), 0.70 (3H, s, Me-25); for ^1H NMR data on the sugar moieties, see table 2; for ^{13}C NMR (C_5D_5N-d_5, 125 MHz) data, see table 1; negative ESIMS *m/z* 1279 $[M - H]^-$; HR-FAB-MS *m/z* 1303.5918 $[M + Na]^+$ (calculated for $C_{60}H_{96}O_{29}Na$, 1303.5935).

3.3.2 Compound 2. white amorphous powder (MeOH–H_2O, 9:1), mp 230–232°C, $[\alpha]_D^{20}$ − 5.20 (c 0.50, MeOH); IR (KBr)v_{max} cm^{-1} 3440 (OH), 2960, 2870, 1730, 1720, 1475, 1330, 1210, 1060, 950 cm^{-1}; ^1H NMR (C_5D_5N-d_5, 500 MHz) δ 6.14 (1H, d, $J = 5.0$ Hz, H-16), 4.58 (1H, dd, J = 6.5, 7.0 Hz, H-22), 3.12 (1H, dd, $J = 4.5$, 11.5 Hz, H-3), 2.04 (3H, s, acetate Me), 1.24 (3H, s, Me-27), 1.15 (3H, s, Me-23), 0.93 (3H, s, Me-24), 0.91 (3H, s, Me-26), 0.87 (3H, s, Me-29), 0.83 (3H, s, Me-30), 0.71 (3H, s, Me-25); for ^1H NMR data of the sugar moieties, see table 2; for ^{13}C NMR (C_5D_5N-d_5, 125 MHz) data, see table 1; positive ESIMS *m/z* 1317 $[M + Na]^+$; HR-FAB-MS *m/z* 1317.5985 $[M + Na]^+$ (calculated for $C_{61}H_{98}O_{29}Na$, 1317.6102).

3.3.3 Acid hydrolysis of 1 and 2. Compounds **1** and **2** (each 5 mg) were refluxed with 5% HCl in MeOH (10 mL) for 5 h; each mixture was diluted with H_2O, then neutralized with Na_2CO_3. The neutral hydrolysate revealed the presence of xylose, glucose, arabinoseand rhamnose by HPTLC [CH_3Cl–MeOH–H_2O (65:35:10) lower layer] when compared with authentic samples (Sigma).

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