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Two Novel Saponins from *Lysimachia capillipes*

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Abstract: Two new saponins named capilliposide C **1** and capilliposide D **2** were isolated from the whole plants of *Lysimachia capillipes,* their structures were determined by 1D and 2D NMR, ESI-MS techniques, and chemical methods. Capilliposide C showed significant cytotoxic activity against human A2780 cells.

Keywords: *Lysimachia capillipes*, triterpene saponin, capilliposide C and D.

We have isolated some flavones, lactone and two new saponins from *Lysimachia capillipes*[1-3], now we continue to report the isolation and structural elucidation of two novel saponins, capilliposide C **1** and capilliposide D **2**. Capilliposide C showed significant cytotoxic activity against human A2780 cells.

The whole plant of *Lysimachia capillipes* was extracted with 95% and 50% EtOH, successively, and the extracts were combined and concentrated. The residue was chromatographed on silica gel resin column, eluting with petroleum ether, CH_2Cl_2, $(CH_3)_2CO$, MeOH, and 50%EtOH, successively. The MeOH eluent was chromatographed on AB-8 resin column to afford a saponin-rich portion, this portion was separated by silica gel column chromatography, eluting with $CHCl_3$/MeOH (contain 5% H_2O) in a gradient manner. Fraction 7 was separated on ODS C_{18} (35−50 μm) column, using MeOH/ H_2O (57.5:42.5) as eluents; and HPLC (10 μm, 10*250 mm, Alltech) using MeOH/ H_2O (56:44) as eluents to afford **1** (20 mg) and **2** (16 mg).

Compound **1** was an amorphous white powder, mp 239-241℃, $[\alpha]_D^{20}$ -10.0 (c 0.50, pyridine), and gave positive result to Liebermann-Burchard test. The negative ESIMS, showed a *quasi*-molecular ion peak at *m/z* 1161.5[M-H]$^-$, the fragment ion peaks at *m/z* 1029[M-132 (xylose)-H]$^-$, 867[1029-162 (glucose)]$^-$, 705[867-162 (glucose)]$^-$ and 573 [705-132(arabinose)]$^-$, indicated the presence of an arabinose inner unit. The molecular formula of **1** ($C_{57}H_{94}O_{24}$) was deduced from ^{13}CNMR and MS data. The seven tertiary methyl groups (δ_H 1.55, 1.28, 1.14, 1.09, 1.03, 1.02 and 0.77) observed in the ^{1}HNMR and ^{13}CNMR spectrum (δ_C 17.5, 17.7, 19.8, 20.9, 26.7, 29.1 and 34.4). The data showed that compound **1** was a triterpene saponin. Glucose, arabinose and xylose were

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detected after the acid hydrolysis of **1** by HPTLC, comparing with authentic samples (Sigma). All the carbon signals were assigned by 2D NMR including ^{1}H-^{1}HCOSY, HMQC-TOCSY and HMBC experiments (**Table 1**), the ^{13}CNMR data were compared with that of anagalligenin A-22-acetate (3β,16α,22α,28α-tetrahydroxy-22-acetate-13,28-epoxyoleanane)[4], indicating that the ^{13}CNMR data of the aglycone of **1** were very similar to that of ^{13}CNMR of anagalligenin A -22-acetate, except the signals of the acetyl in anagalligenin A-22-acetate were replaced by those of isovaleryl in **1**, and the chemical shift of C-3 of **1** shifted downfield by 12.2 ppm, which indicated that the glycoside linked at C-3.

The sugar sequence of the oligosaccharide chain and the glycosidic site of **1** were determined by HMBC spectrum. In the HMBC spectrum (**Figure 1**), the anomeric proton of arabinose at δ_H 4.72(d, 1H, J=6.0 Hz) correlated with C-3 of the aglycone at δ 90.4, the anomeric proton of glucose-I at t δ_H 5.43(d, 1H, J=8.0 Hz) correlated with C-2 of the arabinose at δ_C 80.5, the anomeric proton of glucose-II at δ_H 4.88(d, 1H, J=8.0Hz) correlated with C-4 of the arabinose at δ_C 80.1, the anomeric proton of the xylose at δ_H 4.82(d, 1H, J=7.5 Hz) correlated with C-2 of the glucose-II at δ_C 86.3, the sugar linkages of the oligosaccharide chains were shown in **Figure 1**.

Thus, the structure of the compound **1** was established as 22-isovalerateanagalligenin A, 3-*O*-β-D-xylpyranosyl-(1→2)-β-D-glucopyranosyl-(1→4)-[β-D-glucopyranosyl-(1→2)] -α-L-arabinpyranoside, named as capilliposide C.

Compound **2** was a white amorphous powder, mp 208-210℃, $[\alpha]_D^{20}$ -5.0 (c 0.10, pyridine). The negative ESIMS showed a *quasi*-molecular ion peak at *m/z* 1239.8[M - H]$^-$. The molecular formula ($C_{58}H_{96}O_{28}$) was deduced from ^{13}CNMR and MS data. The NMR data of **2** were very similar to those of **1** (**Table 1**), except for that the signals of the isovaleryl of **1** were replaced by those of *β*-D-glucopyranoside of **2**. Thus the structure of **2** was determined as anagalligenin A, 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 D.

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

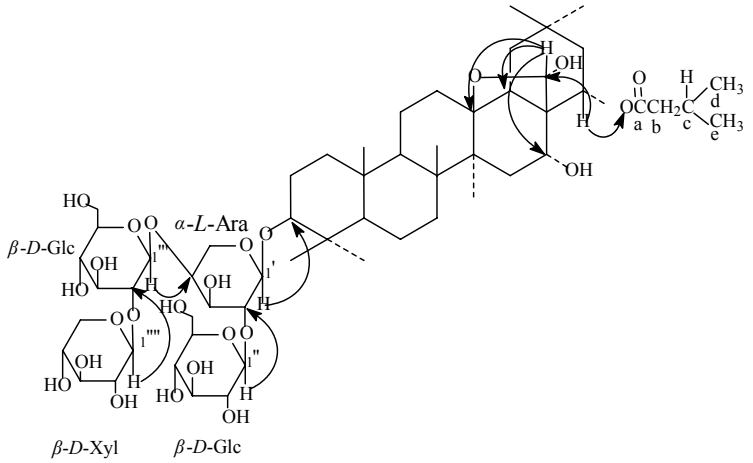

Figure 2 Structure and key HMBC correlations of compound **2**

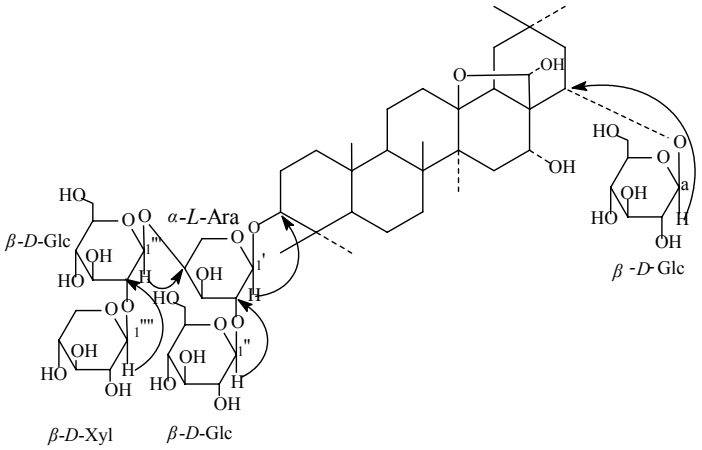

Table 1 The ^{13}CNMR(125MHz) spectral data of compound **1**and **2** (in pyridine-d_6,δppm)

position	**1**	**2**	position		**1**	**2**
1	40.3	38.9	3-O-ara	1'	105.6	104.5
2	27.3	26.3		2'	80.5	79.1
3	90.4	89.0		3'	74.5	73.5
4	40.9	39.5		4'	80.1	78.7
5	56.8	55.4		5'	65.8	64.2
6	19.1	17.6	glc(1→2)	1"	105.9	104.2
7	35.4	34.0		2"	77.1	75.6
8	43.8	43.7		3"	78.6	77.2
9	51.4	50.0		4"	72.8	71.2
10	38.0	36.5		5"	79.2	77.7
11	20.4	19.4		6"	64.0	62.1
12	34.4	33.0	glc(1→4)	1"'	105.4	104.0
13	88.9	87.2		2"'	86.3	84.9
14	45.0	44.1		3"'	79.0	77.2
15	37.8	36.2		4"'	72.0	70.6
16	70.9	69.0		5"'	78.3	77.6
17	52.6	52.4		6"'	63.2	61.8
18	48.5	47.1	xyl(1→2)	1""	108.6	107.2
19	39.5	38.6		2""	77.0	75.7
20	34.5	32.9		3""	79.2	77.2
21	42.8	41.8		4""	71.7	70.3
22	73.8	76.9		5""	68.5	67.1
23	29.1	27.7	At 22-C	a	173.9	103.6
24	17.7	16.3		b	27.7	75.7
25	17.5	18.1		c	45.3	77.6
26	19.8	18.3		d	23.7	71.4
27	20.9	19.8		e	23.6	78.1
28	98.9	97.1		f		62.6
29	34.4	33.3				
30	26.7	25.5				

The cytotoxic activity of compound **1** and **2** were tested against human A2780 cells, compound **1** showed significant cytotoxic activity with IC_{50} value of 0.1 μg/mL but **2** is inactive.

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