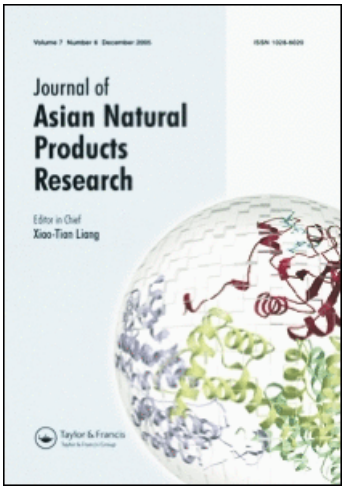

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Two triterpenes from *Lysimachia foenum-graecum*

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One new oleane-type triterpene saponin, named lysimachiagenoside A (**1**) and the known 21-*O*-angeloylbarringtogenol C (**2**) were isolated from the aerial parts of *Lysimachia foenum-graecum* Hance. 21-*O*-angeloylbarringtogenol C was a new natural product. These structures were identified on the basis of 1D- and 2D-NMR techniques, including $^{1}H-^{1}H$ COSY, HMQC, HMBC, TOCSY, and ROESY experiments as well as chemical methods.

Keywords: *Lysimachia foenum-graecum* Hance; triterpene saponin; lysimachiagenoside A

1. Introduction

Lysimachia foenum-graecum Hance (Primulaceae), distributed mainly in Guangxi and Yunnan Provinces of China, has been commonly used as perfume plant and pest repellent. In Chinese folk medicine, the plant has also been used for the treatment of cold and headache [1]. It has been reported that some plants of the genus *Lysimachia* contained saponins and flavones [2–6]. In our recent study, lysimachiagenoside A and 21-*O*-angeloylbarringtogenol C were first isolated from the aerial parts of *L. foenum-graecum*. Lysimachiagenoside A was a new oleanane-type triterpenoid saponin and 21-*O*-angeloylbarringtogenol C was a new natural product. Their structures were identified by 1D- and 2D-NMR techniques. In this paper, we described the isolation and structural elucidation of these two triterpenoid saponins.

2. Results and discussion

Compound **1** was obtained as a white powder. The ESI-MS of **1** showed a pseudo-molecular ion $[M+Na]^+$ at *m/z* 1115.6, compatible with the molecular formula $C_{53}H_{88}O_{23}$, which was further determined by HR-FAB-MS at *m/z* 1115.5574 $[M+Na]^+$. Briefly, the analysis of the NMR spectral data indicated that **1** was a saponin consisting of a triterpene aglycone and four monosaccharides. The ^{13}C NMR spectrum of **1** showed 53 carbon signals, from which 23 were assigned to four monosaccharide units and 30 to triterpene aglycone moiety (Table 1). Detailed comparison of the ^{13}C and ^{1}H NMR spectral data of **1** with those reported in the literature suggested that the aglycone of **1** was barringtogenol C [7]. Four monosaccharide units were determined from the TOCSY spectrum with the aid of COSY, HMQC, and

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HMBC spectra. Starting from the anomeric proton signal at δ_H 5.39 (1H, d, $J = 7.6$ Hz), six correlated carbon signals were observed in the TOCSY spectrum and determined in sequence to be at δ_C 105.4 (C-1), 74.8 (C-2), 79.5 (C-3), 71.7 (C-4), 78.1 (C-5), and 62.8 (C-6), which suggested a glucosyl group. Similarly, another glycosyl group was identified from the analysis of the TOCSY spectra. A 6-deoxymonosaccharide, a rhamnosyl moiety, was elucidated from the methyl carbon at δ_C 18.9 and the corresponding methyl proton at δ_H 1.79 (1H, d, $J = 5.8$ Hz), together with the carbon signals at δ_C 68.8 (C-5), 74.0 (C-4), and 72.7 (C-3). The remaining five carbon signals suggested the presence of a pentosyl group whose anomeric proton at δ_H 4.94 (1H, brs) was only correlated to four carbon signals at δ_C 103.5 (C-1), 80.8 (C-2), 72.1 (C-3), and 74.6 (C-4) in TOCSY spectrum, implying an arabinosyl group. The oxygen-bearing methylene at δ_C 64.2 was assigned to be at the C-5 position of arabinosyl group based on $^1H—^1H$ COSY and HMBC experiments. The above inferences for the monosaccharide unit were further confirmed by TLC analysis of the acid hydrolysate of compound **1**. The glycosidic position of the aglycone was determined to be at the C-3 position on the basis of HMBC correlation between the anomeric proton of arabinosyl group at δ_H 4.94 (1H, brs) with C-3. The connectivity among the monosaccharide units was established with the following HMBC correlations: H-1 (δ_H 5.39) of inner glucosyl group with C-2 (δ_C 80.8) of arabinosyl group; H-1 (δ_H 5.24) of outer glucosyl group with C-4 (δ_C 74.6) of arabinosyl group; and H-1 (δ_H 6.45) of rhamnosyl group with C-2 (δ_C 77.4) of inner glucosyl group. The anomeric configurations of two glucosyl groups were determined to be β-orientated from the coupling constants of the anomeric protons. Similarly, the anomeric protons of rhamnosyl and arabinosyl groups were found to be in the α-orientation (Table 2). Thus, the complete structure of **1** was elucidated as barringtogenol C-3-*O*-α-rhamnopyranosyl (1 → 2)-β-glucopyranosyl

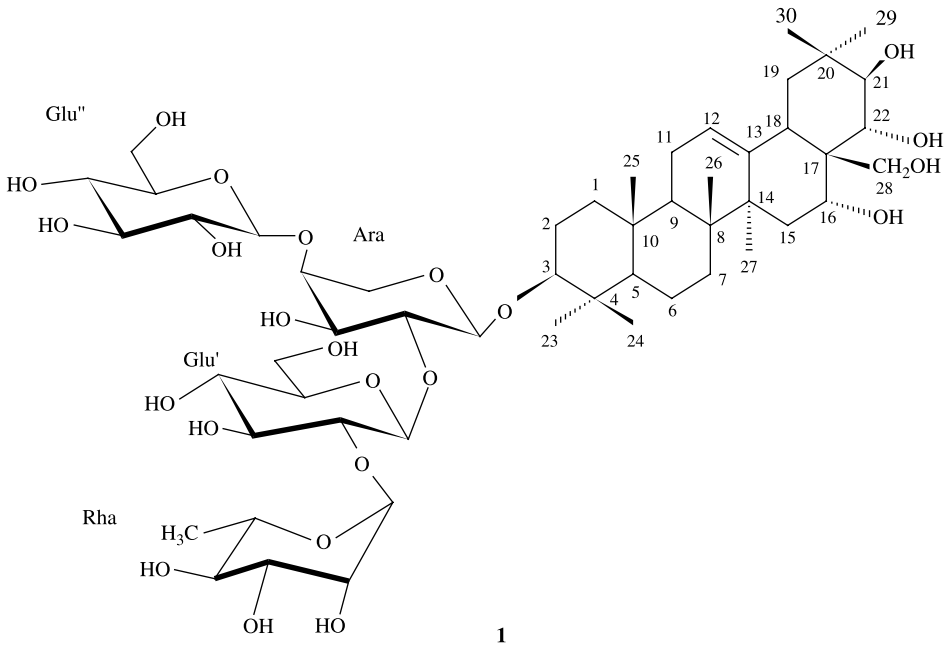
Table 1. ^{13}C NMR spectral data of compounds **1** and **2** (500 Hz).

C No.	**1**[a]	**2**[b]	C No.	**1**	**2**
1	38.2	38.6	1′		169.9
2	25.7	27.0	2′		128.0
3	88.4	78.9	3′		138.5
4	39.4	38.7	4′		15.9
5	55.1	55.1	5′		20.5
6	17.8	18.3	Ara-1	103.5	
7	33.0	32.7	2	80.8	
8	39.9	39.7	3	72.1	
9	46.4	46.5	4	74.6	
10	36.7	36.9	5	64.2	
11	23.2	23.4	Glc′-1	102.5	
12	123.2	123.8	2	77.4	
13	135.6	141.5	3	76.6	
14	41.9	41.4	4	71.2	
15	33.7	33.7	5	78.0	
16	68.0	67.7	6	62.5	
17	48.1	46.9	Glc″-1	105.4	
18	40.5	40.9	2	74.8	
19	47.5	46.7	3	79.5	
20	36.4	35.3	4	71.7	
21	76.3	80.9	5	78.1	
22	76.5	78.6	6	62.8	
23	27.6	28.0	Rha-1	101.5	
24	16.0	15.6	2	72.3	
25	15.0	15.6	3	72.7	
26	16.3	16.7	4	74.0	
27	26.7	27.1	5	68.8	
28	68.2	66.5	6	18.9	
29	30.0	29.3			
30	20.2	19.8			

[a] **1** in pyridine-d_5.
[b] **2** in DMSO.

Table 2. ^1H NMR spectral data for the sugar moiety of compound **1** (125 Hz, pyridine-d_5).

H No.	**1**	H No.	**1**
Ara-1	4.94 (brs)	Glc″-1	5.24 (d, 7.5)
2	4.55	2	4.17
3	4.69	3	4.16
4	4.26	4	4.13
5	4.32, 3.78	5	3.80
		6	4.45, 4.37
Glc′-1	5.39 (d, 7.6)	Rha-1	6.45 (brs)
2	4.04	2	4.51
3	4.29	3	4.59
4	4.16	4	4.53
5	4.09	5	5.00
6	4.35, 4.24	6	1.79 (d, 5.8)



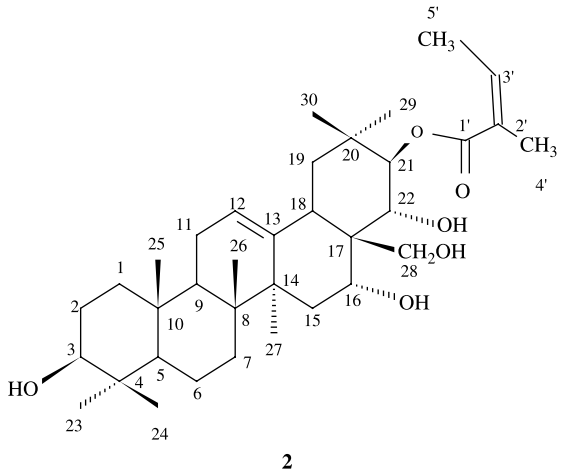


Figure 1. Structures of compounds **1**–**2**.

(1 → 2)-[β-glucopyranosyl (1 → 4)]-α-arabinopyranoside, named lysimachiagenoside A (Figure 1).

Compound **2** was obtained as a white powder. Its molecular formula $C_{35}H_{56}O_6$ was deduced from HR-FAB-MS at *m/z* 595.3979 $[M+Na]^+$. The structure of **2** (Figure 1) was determined to be 21-*O*-angeloylbarringtogenol C by the comparison with the reported spectral data [7], which was first found in natural products.

3. Experimental

3.1 General experimental procedures

Melting points were determined on a K micromelting point apparatus and are uncorrected. MS and HR-MS were obtained

using ESQUIRE-LC or APEXII FT-ICRMS instruments. Optical rotations were determined with a Perkin-Elmer model 241 polarimeter. The IR spectra were run on a Nicolet Impact 400 grating infrared spectrophotometer. The UV spectra were taken on a Perkin-Elmer-554 spectrometer. The 1D- and 2D-NMR spectra were recorded with a BRUKER IVANCE 500 spectrometer. Chemical shifts (δ) are given with TMS as an internal standard. Silica gel precoated plates (Qingdao Ocean Chemical Co., Qingdao, China) were used in TLC. Detection was carried out by spraying with 10% H_2SO_4 solution followed by heating.

3.2 Plant material

The aerial plants of *L. foenum-graecum* were collected in Kunming City, Yunnan Province of China, in June 2001, and were identified by Prof. Zhang Ji. A voucher specimen (No. 0108127) is deposited in the Institute of Chinese Materia Medica, National Institute for the Control of Pharmaceutical and Biological Products.

3.3 Extraction and isolation

The aerial parts of *L. foenum-graecum* (3.0 kg) were extracted with 70% EtOH (2 × 52 l) under reflux. The combined filtrate was divided into petroleum ether, CH_2Cl_2, and remaining ethanol fractions. The CH_2Cl_2 fraction (45 g) was purified by repeated silica gel column chromatography (¢ 9 × 120 cm) eluted with a $CHCl_3$—MeOH (85:15) gradient system and ODS HPLC (MeOH—H_2O, 9:1) to give compound **2** (6 mg). The remaining ethanol fractions (160 g) were absorbed on a Diaion SP825 column, and then sequentially eluted with H_2O and EtOH. The fraction eluted with 50% EtOH (25 g) was subjected to silica gel column chromatography (¢ 7 × 100 cm) using $CHCl_3$—MeOH gradient system to yield fractions I–VIII. Fraction II was purified by repeated silica gel column chromatography and a reversed-phase column (Rp18, ¢ 3.5 × 60 cm) using 65% MeOH as eluent to give compound **1** (7 mg).

3.3.1 *Lysimachiagenoside A (**1**)*

White powder, $[\alpha]_D^{24}$ −3.6 (c = 0.14, MeOH); UV (MeOH) λ_{max} (nm) (log ε): 205 (4.00); IR (KBr) ν_{max} (cm^{-1}): 3441 (OH) and 1239 (C═C); ESI-MS *m/z*: 1115.6 $[M+Na]^+$; HR-FAB-MS *m/z*: 1115.5574 $[M+Na]^+$ (calcd for $C_{53}H_{88}O_{23}Na$, 1115.5614).

3.3.2 *21-O-angeloylbarringtogenol C (**2**)*

White powder, $[\alpha]_D^{24}$ −21.6 (c = 0.14, MeOH); UV (MeOH) λ_{max} (nm) (log ε): 204 (4.14); IR (KBr) ν_{max} (cm^{-1}): 3430 (OH), 1715 (C═O) and 1254 (C═C); ESI-MS *m/z*: 595 $[M+Na]^+$; HR-FAB-MS *m/z*: 595.3979 $[M+Na]^+$ (calcd for $C_{35}H_{56}O_6Na$, 595.3976).

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