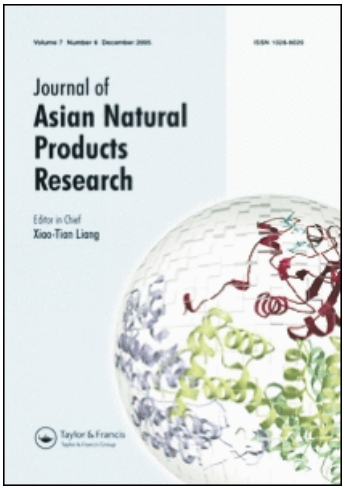

Journal of Asian Natural Products Research
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

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To cite this Article Xu, Fu-Quan , Zhong, Hui-Min , Liu, Hai-Yang , Liu, Hai-Qing and Chen, Chang-Xiang(2007) 'Steroidal saponins from *Lysimachia Paridiformis*', Journal of Asian Natural Products Research, 9: 6, 493 — 497
To link to this Article: DOI: 10.1080/10286020600727434
URL: http://dx.doi.org/10.1080/10286020600727434

Journal of Asian Natural Products Research, Vol. 9, No. 6, September 2007, 493–497

Steroidal saponins from *Lysimachia Paridiformis*

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(Received 2 October 2005; revised 15 February 2006; in final form 22 February 2006)

A new steroidal saponin, paridiformoside B (**1**), was obtained from the EtOH extract of the whole plant of *Lysimachia Paridiformis* Franch, togerher with one steroidal sapogenin (**7**) and seven known steroidal saponins (**2**-**6**, **8**-**9**). Their structures were elucidated using extensive spectroscopic techniques including 1D and 2D NMR spectra.

Keywords: *Lysimachia Paridiformis* Franch; Steroidal saponin; Paridiformoside B

1. Introduction

The genus *Lysimachia* is widely distributed in China, about forty species of this genus are used for detoxication and to treat menstrual disorder and high blood pressure. Some triterpenoid saponins and flavonoid glycosides were isolated from them [1–2]. *Lysimachia paridiformis* Franch has been used in Chinese folk medicine for stopping bleeding. A triterpene saponin which can excite the womb has been reported [3]. During our studies in this plant, eight steroidal saponins and a steroidal sapogenin were obtained and identified as (25*R*)-3-*O*-[β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranosyl-(1 → 4)-β-D-galactopyranosyl]-5α-spirost-9 (11)-en-12-one (**1**), (25*R*)-3-*O*-[β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranosyl-(1 → 4)-β-D-galactopyranosyl]-spirost-5-en-12-one (**2**) [4], (25*R*)-3-*O*-[β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranosyl-(1 → 4)-β-D-galactopyranosyl]-5α-spirost-12-one (**3**) [5–6], (25*R*)-3,6-di-*O*-(β-D-glucopyranosyl)-5α-spirost-3β, 6α,23α-triol (**4**) [7], (25*R*)-6-*O*-(β-D-glucopyranosyl)-5α-spirost-3β,6α-diol (**5**) [8], (25*R*)-3,6-di -*O*-(β-D-glucopyranosyl)-5α-spirost-3β,6α-diol (**6**) [9], (25*R*)-5α-spirost-3β,6α,23α-triol (**7**) [10], β-sitosterol (**8**) and daucosterol (**9**).

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Journal of Asian Natural Products Research
ISSN 1028-6020 print/ISSN 1477-2213 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/10286020600727434

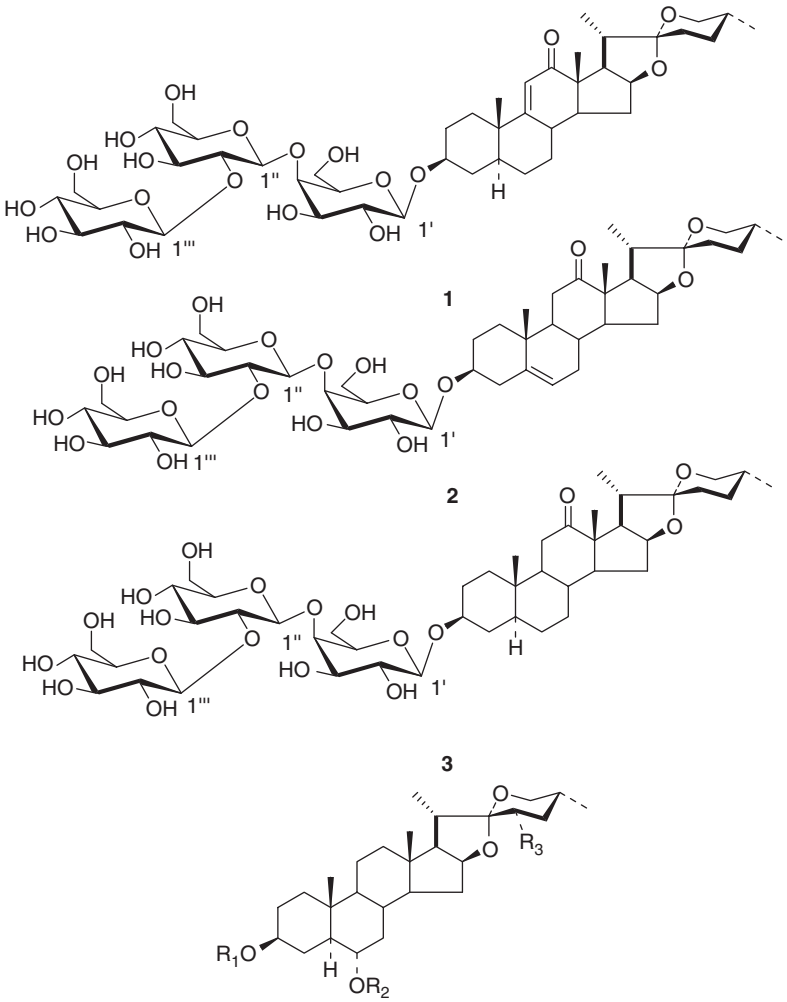

Figure 1. Structures of compounds **1**–**7**.

2. Results and discussion

Compound **1** was obtained as white amorphous powder. The negative HRESIMS of **1** gave an $[M - H]^-$ peak at *m/z* 913.4428, corresponding to a molecular formula of $C_{45}H_{70}O_{19}$. The IR spectrum gave characteristic absorption bands at ν_{max} 3425 (hydroxyl groups), 981, 921, 898 and 866 cm^{-1} (intensity 898 > 921 cm^{-1}), suggested the presence of a (25*R*)-spirostanol steroidal skeleton in the aglycone. The IR spectrum exhibited absorption for carbonyl (1675 cm^{-1}) and olefinic groups (1598 cm^{-1}) showing an α, β–unsaturated ketone, which was confirmed by the UV spectrum at λ_{max} 239 nm.

The ^{13}C NMR spectrum of aglycone moiety of **1** showed signals for four methyls, nine methylene carbons, nine methine including two oxymethine carbon [δ 80.3 (C-16), 76.7

(C-3)], and five quaternary carbons [δ 204.5 (C-12), 171.4 (C-9), 109.5 (C-22), 51.4 (C-13), 39.5 (C-10)]. The ^{1}H NMR spectrum of **1** showed two methyl singlets at δ 0.81 (H-18) and 1.00 (H-19) and two methyl doublets at δ 0.70 ($J = 4.5$ Hz, H-27) and 1.40 ($J = 6.5$ Hz, H-21) for the spirostanol skeleton, as well as three anomeric protons. In addition, the DEPT spectrum exhibited a characteristic carbonyl group signal at δ 204.5 (C-12) and olefinic carbon signals at 171.4 (C-9), 120.0 (C-11). Comparison of the ^{1}H and ^{13}C NMR spectral data of **1** with those of 3β-hydroxy-5α-spirost-9 (11)-en-12-one [11], showed that the two structures were very similar expect that **1** had an additional sugar moiety.

In the negative-ion FABMS, the significant fragment ion peaks at *m/z* 751 [M − H − 162 (hexosyl)]$^-$, and 589 [M − H − 162 (hexosyl) − 162 (hexosyl)]$^-$ suggested the presence of two hexosyl units in the molecule of **1**. In the ^{1}H NMR spectrum of **1,** three anomeric proton signals at δ 4.90 (1H, d, $J = 7.5$ Hz), 5.14 (1H, d, $J = 7.6$ Hz), 5.22 (1H, d, $J = 7.8$ Hz), and the signals at δ 102.5, 105.2, and 107.0 in the HMQC indicated the occurrence of three sugar residues. The ^{13}C NMR data of the sugar moiety were very close to those of the co-curring known compound **2**, suggesting that both compounds had the same sugar linkages. The HMBC, ^{1}H–^{1}H COSY, and ROESY spectra confirmed the sugar linkage sesquence. In the HMBC spectrum of **1**, the correlations of H-1′ with C-3, H-1″ with C-4′, H-1‴ with C-2″ were observed. Thus, **1** was determined as (25*R*)-3-*O*-[β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranosyl-(1 → 4)-β-D-galactopyranosyl]-5α-spirost-9 (11)-en-12-one.

3. Experimental

3.1 General experimental procedures

Melting points were measured on the Koffler melting apparatus produced by Sichuan University (China) and are uncorrected. FABMS were recorded on a VG Auto spec-3000 spectrometer and HR-ESIMS were recorded on an API Qstar Pulsar instrument. All NMR experiments were recorded on a Bruker DRX-500 spectrometer at room temperature. IR spectra were carried on a Bio-Rad FTS-135 spectrometer with KBr pellets. Optional rotations were measured on a SEPA-3000 automatic digital polarimeter and UV spectra were obtained on a Shimadzu double-beam 210 A spectrophotometer.

3.2 Plant material

The whole plant of *Lysimachia paridiformis* Franch was collected from Enshi, Hubei province (China) in June 2004 and identified by professor R. C. Fang and X. D. Li at Kunming

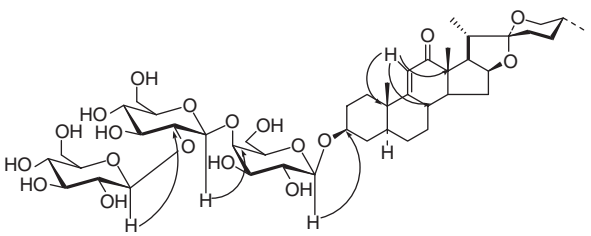

Figure 2. Significant HMBC correlations of **1**.

Institute of Botany, the Chinese Academy of Sciences, Kunming, Yunnan, China, where a voucher specimen (NO.0806718) is deposited.

3.3 Extraction and isolation

The whole plant (5.0 kg) was extracted with 75% EtOH (3 × 3 h) under reflux. After evaporation of ethanol *in vacuo*, the concentrated extract was suspended in water and extracted successively with EtOAc and n-BuOH. The n-BuOH fraction (214 g) was subjected to silica gel column chromatography eluted with $CHCl_3$-MeOH to obtain four fractions. Fraction I was repeatedly subjected to silica gel column chromatography eluted with $CHCl_3$-MeOH, and to Rp-18 column chromatography eluted with aqueous MeOH yielding **4** (90 mg); by the same methods, **6** (9 mg) was obtained from fraction II; **5** (11 mg) and **7** (54 mg) were isolated from fraction IV. The compounds **1** (8 mg), **2** (6 mg) and **3** (30 mg) were obtained by semipreparative reversed phase HPLC with MeOH-H_2O (70:30) from fraction II.

3.3.1 (25*R*)-3-*O*-[β-D-glucopyranosyl-(1 → 2)-β-D-glucopyranosyl-(1 → 4)-β-D-galactopyranosyl]-5α-spirost-9(11)-en-12-one (1). $C_{45}H_{70}O_{19}$. White amorphous powder. mp 193–195°C. $[\alpha]_D^{20}$ − 24.3(*c* 0.055, C_5H_5N). IR (KBr) ν_{max} (cm^{-1}): 3425, 1674, 1598, 981, 921, 898, 866 (intensity 898 > 921). Negative FABMS *m/z*: 913 $[M - H]^-$, 751 $[M - H - 162]^-$, 589 $[M - H - 162 - 162]^-$. Negative HRESIMS *m/z*: 913.4428

Table 1. ^{13}C NMR data of compounds **1-3** (C_5D_5N).

Aglycone	*1*	*2*	*3*	*Sugar*	*1*	*2*	*3*
1	35.0	37.1	36.7	gal-1′	102.5	102.8	102.4
2	29.8	30.0	29.8	2′	73.3	73.3	73.3
3	76.7	77.7	77.7	3′	75.2	75.6	75.2
4	34.7	39.1	34.7	4′	81.1	80.9	81.0
5	42.5	140.9	44.5	5′	75.6	75.2	75.7
6	27.9	121.4	28.6	6′	60.7	60.6	60.6
7	32.6	31.6	31.8	glc-1″	105.2	105.2	105.3
8	36.9	30.9	34.4	2″	86.2	86.1	86.2
9	171.4	53.4	55.9	3″	78.5	78.2	78.5
10	39.5	37.6	36.3	4″	71.9	71.9	71.9
11	120.0	37.6	38.0	5″	78.2	78.5	78.2
12	204.5	213.2	212.9	6″	63.2	63.3	63.3
13	51.4	55.0	55.4	glc-1‴	107.0	107.0	107.0
14	52.8	56.1	55.5	2‴	76.8	76.8	76.8
15	31.8	31.8	31.5	3‴	79.0	79.8	79.0
16	80.3	79.8	79.7	4‴	70.3	70.4	70.4
17	54.6	54.1	54.3	5‴	77.7	78.0	77.1
18	15.3	15.9	16.2	6‴	61.6	61.7	61.6
19	18.3	18.8	11.8				
20	43.0	42.7	42.7				
21	13.8	13.9	14.0				
22	109.5	109.4	109.4				
23	31.8	31.9	31.7				
24	29.2	29.3	29.3				
25	30.6	30.6	30.6				
26	67.0	67.0	67.0				
27	17.4	17.3	17.4				

$[M - H]^-$ (calcd for $C_{45}H_{69}O_{19}$, 913.4433). ^{1}H NMR (500 MHz, *pyridine-d_5*) δ 0.70 (3H, d, $J = 4.5$ Hz, Me-27), 0.81 (3H, s, Me-19), 1.00 (3H, s, Me-18), 1.40 (3H, d, $J = 6.5$ Hz, Me-21), 4.90 (1H, d, $J = 7.5$ Hz, H-1′), 5.14 (1H, d, $J = 7.6$ Hz, H-1″), 5.22 (1H, d, $J = 7.8$ Hz, H-1‴), 5.77 (1H, s, H-11). ^{13}C NMR (100 MHz, *pyridine-d_5*) data see Table 1.

Acknowledgements

The authors are grateful to Mr. He Y. N. and Ms. Liang H. L. in the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, for measuring NMR and MS data, respectively.

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