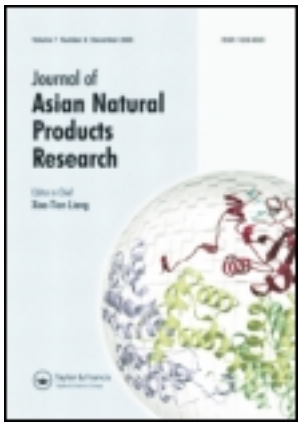

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Two new triterpenoids from Picria fel-terrae

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Two new triterpenoids from *Picria fel-terrae*

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Two new triterpenoids, picfeltarraegenin VII (**1**) and picfeltarraenin X (**2**), have been isolated from *Picria fel-terrae* Lour., along with three known ones, picfeltarraegenin VI (**3**), picfeltarraenins VI (**4**) and VII (**5**). Their structures have been elucidated by means of spectroscopic methods.

Keywords: *Picria fel-terrae* Lour; Scrophulariaceae; Triterpenoid; Picfeltarraegenin VII; Picfeltarraenin X

1. Introduction

Picria fel-terrae Lour., belonging to the genus *Picria* (Scrophulariaceae), has been used as a Chinese folk medicine for its anti-inflammatory properties [1]. Many triterpenoids have been isolated from *P. fel-terrae* [2–5], and four of them exhibited complement-inhibiting properties that could partly explain its traditional use in treating inflammation [6]. Our further studies have led to the isolation of five triterpenoids, including two new ones named picfeltarraegenin VII (**1**) and picfeltarraenin X (**2**). Herein we report their isolation and structural elucidation.

2. Results and discussion

Compound **1** was obtained as colorless needles, mp 231–233°C. The IR spectrum shows the presence of hydroxyl groups at 3442 cm^{-1}, carbonyl groups at 1689 cm^{-1}, and an olefinic group at 1632 cm^{-1}. Its molecular formula, $C_{30}H_{46}O_7$, was determined by positive HRFAB-MS, *m/z* 541.3150 $[M + Na]^+$. This is confirmed by the ^{13}C NMR and

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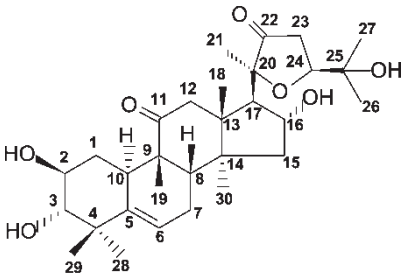
Table 1. NMR data of **1**–**3**[a].

	1		***2***		***3***
Position	*^{1}H(J in Hz)*	*^{13}C*	*^{1}H (J in Hz)*	*^{13}C*	*^{13}C*
Aglycon					
1	2.43 m	34.7	2.55 m	33.5	34.7
	1.45 overlap		1.56 overlap		
2	4.08 m	71.0	4.32 m	83.4	71.0
3	3.41 d (8.0)	81.5	3.53 d (8.8)	80.8	81.5
4		42.8		42.6	42.9
5		142.5		141.7	142.5
6	5.68 t (6.0)	118.6	5.69 t (6.0)	118.9	118.7
7	2.31 dd (6.0, 13.0)	24.1	2.31 dd (6.0, 13.4)	24.2	24.2
	1.89 m		1.89 overlap		
8	1.85 overlap	43.5	1.85 overlap	43.3	43.4
9		48.3		48.2	48.2
10	2.69 br d (12.6)	34.4	2.78 br d (12.4)	34.2	34.4
11		213.3		212.8	213.0
12	3.18 overlap	48.9	3.07 d (14.5)	48.7	48.8
	2.69 d (12.6)		2.51 d (7.0)		
13		48.9		48.9	48.9
14		50.5		50.6	50.7
15	1.85 overlap	46.5	1.90 overlap	46.5	46.6
	1.68 br d (12.8)		1.70 br d (12.0)		
16	5.37 t (8.0)	70.2	4.74 t (8.0)	69.8	69.8
17	2.88 d (8.0)	59.4	2.95 d (8.0)	59.2	59.2
18	1.04 s, 3H	20.0	0.93 s, 3H	20.1	20.2
19	1.20 s, 3H	20.5	1.16 s, 3H	20.3	20.5
20		84.3		91.0	91.0
21	1.41 s, 3H	20.7	1.53 s, 3H	23.1	23.3
22		217.4		206.8	206.9
23	3.22 dd (11.2, 17.0)	38.0	5.11 s	101.1	101.2
24	4.55 dd (5.5, 11.2)	80.0		195.2	195.3
25		69.9	2.60 m (6.8)	30.3	30.4
26	1.54 s, 3H	26.3	1.04 d (6.8), 3H	19.6	19.7
27	1.35 s, 3H	27.4	1.07 d (6.8), 3H	19.4	19.4
28	1.43 s, 3H	25.5	1.30 s, 3H	25.3	25.5
29	1.26 s, 3H	22.4	1.42 s, 3H	22.2	22.4
30	1.45 s, 3H	19.4	1.47 s, 3H	18.9	19.0
Glucosyl					
1			5.30 d (8.0)	106.5	
2			4.20 t (8.0)	78.5	
3			4.10 t (8.0)	76.0	
4			4.30 overlap	71.3	
5			3.85 m	78.5	
6			4.45 m; 4.37 m	62.5	

[a] ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR in pyridine-d_5. All signals were assigned by ^{1}H–^{1}H COSY, HMQC and HMBC spectra.

DEPT spectra (table 1), which also show the presence of eight methyls, five methylenes, eight methines, nine quaternary carbons. The ^{1}H NMR spectrum of **1** exhibits an olefinic proton of triplets at δ 5.68 (1H, t, $J = 6.0$ Hz) and eight tertiary methyl groups (δ 1.04, 1.20, 1.26, 1.35, 1.41, 1.43, 1.45, 1.54). All these spectral data suggest **1** is a triterpenoid-like picfeltarraegenin II [7] and picfeltarraegenin VI [8]. Comparison of NMR data indicates that compound **1** is 2-hydroxypicfeltarraegenin II. This was confirmed by the ^{1}H–^{1}H COSY correlation of H-2 (δ 4.08) and H-3 (δ 3.41). In addition, the stereochemistry of **1** was determined on the basis of the key NOEs of 10α-H/2α-H and 1β-H/3β-H, and the 2-OH at β orientation is further confirmed by $J_{2\alpha-H,3\beta-H} = 8.0$ Hz. Accordingly, all the 1D and 2D NMR data are well assigned, and the structure of **1** is elucidated to be 11,22-dioxo-

2β,3α,16α,25-tetrahydroxy-(20*S*,24)-epoxycucurbit-5-ene, with a trivial name of picfeltarraegenin VII



1

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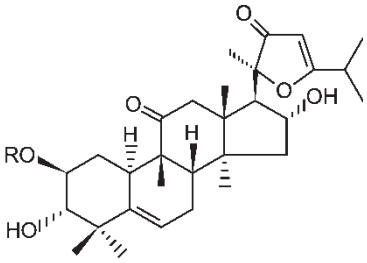
The FAB-MS of compound **2** shows a pseudo-molecular ion $[M-H]^-$ at *m/z* 661, compatible with the molecular formula $C_{36}H_{54}O_{11}$, which was further determined by HRFAB-MS, *m/z* 661.3582 $[M-H]^-$. A characteristic fragment ion in the FABMS spectrum at *m/z* 499 (loss of 162 u) indicates that there is a glucopyranosyl unit in **2**. The ^{13}C NMR spectrum of **2** further indicates that it is a triterpene glycoside, and the aglycone is identical with picfeltarraegenin VI (**3**) [8]. Further comparison of the NMR data (table 1) of **2** and a known glycoside of **3** (picfeltarraenin IX) [5] suggest that **2** might be picfeltarraegenin VI 2-*O*-β-D-glucopyranoside, which was confirmed by the HMBC correlation of H-2 (δ 4.32) with the anomeric carbon (δ 106.5) of the glucose unit and the anomeric proton (δ 5.30, d, $J = 8.0$ Hz) with C-2 (δ 83.4). Finally analysis of the ROESY spectrum of **2** completely supports that it is picfeltarraegenin VI 2-*O*-β-D-glucopyranoside, called picfeltarraenin X.



2R = β-D-glucopyranosyl, **3**R = H

The structures of **3**–**5** were determined to be picfeltarraegenin VI [8], picfeltarraenins VI [6] and VII [5], respectively, by comparison with the reported spectral data.

3. Experimental

3.1 General experimental procedures

Melting points were determined on a XRC-1 micromelting point apparatus and are uncorrected. MS and HRMS were obtained using a VG Auto Spec-3000 or a Finnigan MAT 90 instrument. Optical rotations were determined with a Perkin-Elmer model 241 polarimeter. IR spectra were run on a Bio-Rad FTS-135 grating infrared spectrophotometer.

UV spectra were taken on a UV210A spectrometer. 1D and 2D NMR spectra were recorded with a Bruker AM-400 spectrometer. Chemical shifts (δ) are given with TMS as an internal standard. Silica gel precoated plates (Qingdao Ocean Chemical Co.) were used in TLC. Detection was carried out by spraying with 10% H_2SO_4 solution followed by heating.

3.2 Plant material

The whole plant of *Picria fel-terrae* Lour. was collected in Wuzhou city, Guangxi province of China, in October 2001. A voucher specimen (PF-0101) has been deposited in the herbarium of the testing center of Guilin Sanjin Pharmaceutical Co., China.

3.3 Extraction and isolation

The dried plant (10 kg) was pulverized and successively extracted with EtOH (2×100 L) under reflux. The combined filtrate was then concentrated under reduced pressure and absorbed on a Diaion HP-20 (Mitsubishi Co.) column, and was then sequentially eluted with H_2O and MeOH. The fraction eluted with MeOH was concentrated and chromatographed on a silica-gel column using $CHCl_3$–MeOH mixtures as eluent (increasing polarity, from 19:1 to 1:1) to give 10 fractions (I–X). Fractions III and V were rechromatographed on a silica-gel column with $CHCl_3$–MeOH (15:1 and 10:1) as eluent to give **3** (300 mg) and **2** (320 mg). Fraction IV was rechromatographed on a silica-gel column with $CHCl_3$–MeOH (15:1 to 10:1) as eluent, to afford **1** (85 mg), **4** (1500 mg), and **5** (46 mg), respectively.

Picfeltarraegenin VII (**1**): colorless needles, mp 231–233°C; $[\alpha]_D^{28}$: + 80.2 (*c* 0.137, MeOH); UV (MeOH) λ_{max} (nm) (log ϵ): 229 (3.79); IR (KBr) ν_{max} (cm^{-1}): 3441 (OH), 1688 (C═O), 1631 (C═C); EI-MS *m/z* 518 $[M]^+$; HRFAB-MS *m/z* 541.3150 $[M + Na]^+$ (calcd for $C_{30}H_{46}O_7Na$, 541.3141).

Picfeltarraenin X (**2**): amorphous powder, $[\alpha]_D^{28}$ + 89.6 (*c* 0.212, MeOH); UV (MeOH) λ_{max} (nm) (log ϵ): 261 (4.00). IR (KBr) ν_{max} (cm^{-1}): 3443 (OH), 1690 (C═O), 1630 (C═C); FAB-MS (glycerol) *m/z* 661 $[M - H]^-$, 499 $[M - 162 - H]^-$; HRFAB-MS *m/z* 661.3582 $[M - H]^-$ (calcd for $C_{36}H_{53}O_{11}$, 661.3587).

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