A new picfeltarraenone glycoside from *Picria fel-terrae*

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Abstract: Aim To investigate the chemical constituents from *Picria fel-terme* Lour. **Methods** Column chromatography techniques were used to isolate the chemical constituents, physico-chemical constants and spectroscopic analysis were employed for structural elucidation. **Results** Two triterpenoids named picfeltarraenone I (**1**) and picfeltarraenin XI (**2**) were isolated, and their structures were established to be 3, 11, 22-trioxo-16α-hydroxy-(20*S*, 24)-epoxy-cucurbit-5, 23-diene (**1**) and 3, 11, 22-trioxo-16α-hydroxy-(20*S*, 24)-epoxy-cucurbit-5, 23-diene-2β-*O*-β-*D*-glucopyranoside (**2**), respectively. **Conclusion** Compound **2** is a new compound, the ^{13}CNMR data of compound **1** is reported for the first time.

Key words: *Picria fel-terme*; *triterpenoid*; picfeltarraenin
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苦玄参中一个新苦玄参酮苷的分离与结构鉴定

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摘要: 目的　研究苦玄参的三萜类化学成分。方法　采用大孔树脂、硅胶柱色谱纯化, 经理化常数、光谱学方法鉴定结构。结果　分离得到了2个三萜成分, 分别鉴定为3, 11, 22-三羰基-16α-羟基-(20*S*, 24)-环氧苦味素-5, 23-二烯(**1**)和3, 11, 22-三羰基-16α-羟基-(20*S*, 24)-环氧苦味素-5, 23-二烯-2β-*O*-β-*D*-吡喃葡糖苷(**2**)。结论　化合物**1**为已知化合物苦玄参酮I, 其^{13}CNMR数据为本文首次报导; 化合物**2**为新三萜皂苷。

关键词: 苦玄参; 三萜; 苦玄参苷

Introduction

Picria fel-tarme Lour., an annual plant mainly distributed in southern China, is used as a folk medicine for the treatment of herpes infections, cancer, and inflammation[1]. Many chemical studies on this plant were focused on its triterpenoids[2,3]. In this paper, we report the structural elucidation of a new triterpenoid, picfeltarraenin XI (**2**) from *Picia fel-terme*.

Results and discussion

Compound 1　Colorless needles, mp 218 - 219 ℃. The EIMS showed a molecular ion peak at *m/z* 482[M]$^+$, compatible with the molecular formula $C_{30}H_{42}O_5$, which was supported by ^{13}CNMR and DEPT spectra. The ^{13}CNMR spectrum of **1** showed 30 carbon signals, including three carbonyl carbon signals (δ 206.7, 212.8 and 212.8), four olefinic carbons (δ 101.1 d, 119.8 d, 141.3 s and 195.1 s) and eight methyl carbon resonances. Two olefinic proton signals (δ 5.58 and 5.66) were observed in the ^{1}HNMR spectrum. Interpretation of the ^{13}CNMR and 2D NMR spectral data of **1** (Table 1) led to the identification of **1** as picfeltarraenone I[4].

Compound 2　Amorphous powder, exhibited a quasi-molecular ion peak at *m/z* 659[M - H]$^-$ and a characteristic fragment ion peak at *m/z* 497 (loss of 162 u) in FABMS indicated that there is a

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Table 1 NMR data of compounds 1 and 2[a] (*J* in Hz in parentheses)

No.	2		1
	^{1}H	^{13}C	^{13}C
Aglycone			
1	2.58 m	35.2 t	25.3 t
	1.66 overlap		
2	5.52 m	78.8 d	38.2 t
3		212.6 s	212.8 s
4		51.7 s	48.2 s
5		140.7 s	141.3 s
6	5.75 br s	120.4 d	119.8 d
7	2.31 dd (6.0, 13.0)	24.2 t	24.2 t
	1.75 overlap		
8	1.85 overlap	43.0 d	43.0 d
9		48.2 s	49.2 s
10	3.10 br d (12.0)	34.2 d	35.9 d
11		211.7 s	212.8 s
12	3.00 d (16.0)	48.7 t	48.8 t
	2.52 d (16.0)		
13		48.9 s	50.6 s
14		50.6 s	51.2 s
15	1.90 overlap	46.4 t	46.5 t
	1.70 br d (12.0)		
16	4.75 t (8.0)	69.7 d	69.7 d
17	2.95 d (8.0)	59.1 d	59.2 d
18	0.92 s	19.9 q	19.7 q
19	1.15 s	20.1 q	20.1 q
20		91.0 s	90.9 s
21	1.52 s	23.1 q	23.2 q
22		206.9 s	206.7 s
23	5.65 s	101.2 d	101.1 d
24		195.3 s	195.1 s
25	2.60 m	30.4 d	30.3 d
26	1.05 d (6.0)	19.7 q	19.6 q
27	1.08 d (6.0)	19.4 q	19.4 q
28	1.34 s	28.6 q	28.7 q
29	1.36 s	21.2 q	22.8 q
30	1.43 s	18.6 q	18.7 q
Glucosyl			
1	5.16 d (7.8)	104.1 d	
2	4.22 t (7.8)	75.9 d	
3	4.10 t (7.8)	78.5 d	
4	4.30 overlap	71.3 d	
5	3.86 m	77.9 d	
6	4.50 m; 4.35 m	62.5 t	

[a] 400 MHz and 100 MHz for ^{1}H and ^{13}C NMR in pyridine-d_5. All ^{1}H and ^{13}C NMR signals were assigned by means of ^{1}H-^{1}H COSY, HMQC and HMBC experiments

glucopyranosyl moiety in **2**. Its molecular formula, $C_{36}H_{52}O_{11}$, was determined by HRFABMS, *m/z* 659.341 2 [M - H]$^-$. In UV spectrum the maximum absorption at 261 nm (4.16) suggested the presence of C=C - C=O functionality. The ^{13}C NMR spectrum further indicated that compound **2** was a triterpene glycoside and the aglycone was very similar to **1** (Table 1). The placement of the glucopyranosyl moiety on the aglycone was determined by HMBC spectrum. Long-range correlations were observed between H-2 (δ 5.52) with the anomeric carbon (δ 104.1) of glucose unit, and the anomeric proton (δ 5.16, d, *J* = 7.8 Hz) with C-2 (δ 78.8), indicated that the glucopyranose was located at C-2. The relative stereochemistry of **2** was established on the basis of a ROESY experiment. The cross-peak observed between 10α-H and 2α-H suggested that the glucopyranose at C-2 is in β configuration. Accordingly, all the 1D and 2D NMR data were well assigned, and the structure of **2** was completely established to be 3, 11, 22-trioxo-16α-hydroxy-(20*S*, 24)-epoxy-cucurbit-5, 23-diene-2β-*O*-β-*D*-glucopyranoside, and assigned the trivial name picfeltarraenin XI.

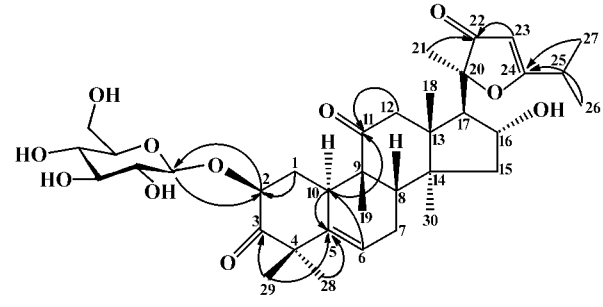

Figure 1 Key HMBC correlations of compound **2**
Arrows point from proton to carbon

Experimental

Melting points were determined on a XRC-1 micromelting point apparatus and were uncorrected. The MS and HRMS were obtained on 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) were given with TMS as an internal standard. Silica gel precoated plates (Qingdao Ocean Chemical Co.) were used in TLC and detection was carried out by spraying with 10% H_2SO_4 ethanol followed by heating.

Plant Material The whole plant of *Picria felterme* Lour. (Scrophulariaceae) was collected in Wuzhou city, China, in 2001. A voucher specimen (PF-0101) is deposited in the herbarium of the test

center of Guilin Sanjin Pharm. Co., China.

Extraction and Isolation Dried and powdered plant material (10 kg) was extracted with EtOH (2 × 100 L) under reflux. The combined filtrate was concentrated under reduced pressure, then subjected to column chromatography (CC) on Diaion HP-20 (Mitsubishi) eluted with H_2O and MeOH. The fraction eluted with MeOH was concentrated and chromatographed on silica gel column, eluted with a $CHCl_3$-MeOH gradient (from 19∶1 to 1∶1), giving 10 fractions. Fraction II was subjected to column chromatography on silica gel repeatedly. Elution with solvent $CHCl_3$-MeOH (9∶1) yielded compound **1** (125 mg). Fraction IV was subjected to repeated column chromatography on silica gel using $CHCl_3$-MeOH (12∶1) as eluent, resulting in the isolation of compound **2** (25 mg).

Picfeltarraenone I (1) Colorless needles, mp 218 - 219 ℃. UV (MeOH) λ_{max} nm (log ε): 260 (4.10) (O=C - C=C). EIMS: *m/z* 482 $[M]^+$. ^{13}CNMR data (C_5D_5N): see table 1.

Picfeltarraenin XI (2) White amorphous powder. $[\alpha]_D^{26}$ +35.9°(c 0.167, MeOH). IR(KBr) ν_{max} cm^{-1}: 3 442 (OH), 1 690 (C=O), 1 585 (C=C - C=O). UV(MeOH) λ_{max} nm (log ε): 261 (4.16). FABMS(glycerol): *m/z* 659 $[M - H]^-$, 645, 629, 497 $[M - 162 - H]^-$. HRFABMS: *m/z* 659.341 2 $[M - H]^-$ (calcd for $C_{36}H_{51}O_{11}$, 659.343 1). ^{1}H and ^{13}CNMR data (C_5D_5N): see table 1.

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