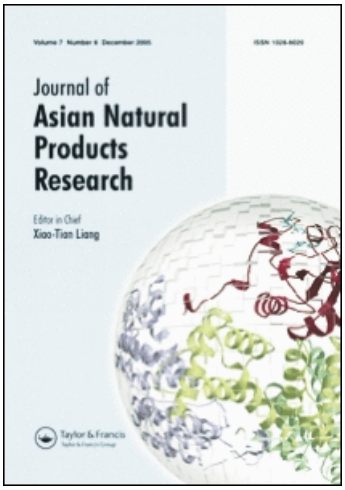

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A new cucurbitacin from *Picria fel-terrae*

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Note

A new cucurbitacin from *Picria fel-terrae*

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A new cucurbitacin, picfeltarraenone II (**1**) as well as four known cucurbitacins, picfeltarraegenin I (**2**), picfeltarraenin IA (**3**), picfeltarraenin IB (**4**), and picfeltarraenin IV (**5**), have been isolated and characterized from the whole plant of *Picria fel-terrae*. The purity of picfeltarraenin IA has been determined by TLC and HPLC.

Keywords: *Picria fel-terrae* Lour.; Picfeltarraenone II; Cucurbitacin; Triterpene

1. Introduction

Picria fel-terrae Lour., an annual plant mainly distributed in the tropical and subtropical regions of Asia, has been included in the *Guangxi Herbal Drugs Pharmacopeia* (1992 version). Triterpenoids isolated from this plant belong to cucurbitacins [1], and which characterized structurally by (20*S*,24)-epoxy rings [2,3]. In the preceding paper, we reported the isolation and structure determination of two new cucurbitacins from the ethanolic extract of *Picria fel-terrae* [4]. As a continuation of our investigation on the constituents of this crude drug, this paper deals with the isolation and structure elucidation of a new cucurbitacin, picfeltarraenone II (**1**). Since the content of picfeltarraenin IA has been used as quality criterion of several Chinese Traditional Patent Medicine containing *Picria fel-terrae* [5], and the authentic sample used as quality control of the herbal medicine of picfeltarraenin IA can not be obtained from the market yet, the isolation and purity analysis of picfeltarraenin IA are introduced.

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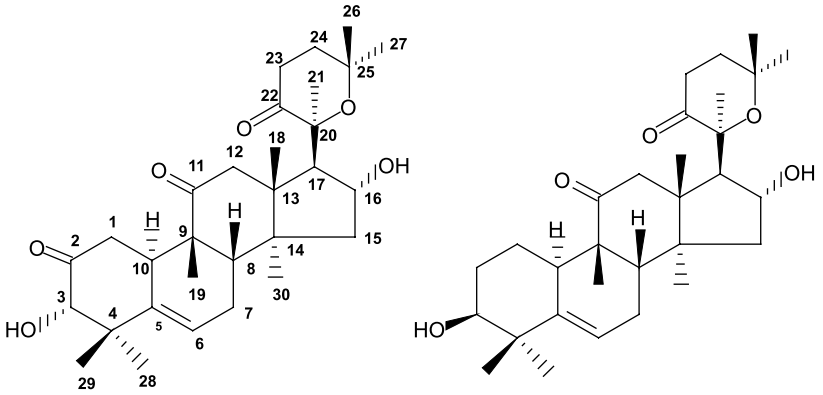
2. Results and discussion

Compound **1**, named picfeltarraenone II, was obtained as colourless needles, molecular formula $C_{30}H_{44}O_6$ determined by HRFAB-MS, *m/z* 501.3229 $[M + H]^+$. Its IR spectrum suggests the presence of hydroxy, carbonyl, and olefinic functionalities, with absorption bands at 3444, 1693, and 1633 cm^{-1}, respectively. The ^1H NMR spectrum indicated the presence of eight methyl groups resonating as singlets and an olefinic proton at δ 5.84 (1H, t, $J = 6.0$ Hz, table 1). The ^{13}C NMR and DEPT spectra of compound **1** exhibited 30 carbon signals, including eight methyls, six methylenes, six methines and ten quaternary carbons. The olefinic carbon signals at δ 121.5 and 139.4 correspond to an endocylic double bond between C-5/C-6. The resonances of oxygenated carbons indicated the presence of two oxymethine carbons (δ 81.1, 70.3; C-3 and C-16), two oxygenated quaternary carbons (δ 80.1, 69.1; C-20 and C-25), and three oxygenated carbonyl carbons (δ 211.0, 212.8, 216.1; C-2, C-11, and C-22). These data suggested the presence of a highly oxygenated C_{30} cucurbitacin. Comparison of the ^1H NMR and ^{13}C NMR data with those of **6** (cordifolin A, from *Fevillea cordifolia*) [6] revealed that the structure of compound **1** is very similar to that

Table 1. NMR data of **1**[a] and **6**, and key HMBC correlations and ROEs of **1**.

No.	***1***			***6***	
	^1H	*^{13}C*	*HMBC*	*ROESY*	*^{13}C*
1	2.61 dd (5.0, 13.0) 2.46 d (13.0)	39.9 t	2, 3, 10	3β	21.7 t
2		211.0 s			29.8 t
3	4.25 s	81.1 d	2, 4, 5, 28, 29	1β, 29	76.9 d
4		47.0 s			42.3 s
5		139.4 s			141.4 s
6	5.84 t (6.0)	121.5 d	5, 7, 8, 10		120.3 d
7	2.35 dd (6.0, 12.4) 1.95 overlap	24.1 t	5, 6, 8		24.8 t
8	1.98 overlap	43.1 d	6, 7, 9, 11	18, 19	44.6 d
9		48.6 s			50.4 s
10	3.02 m	36.6 d	1, 2, 5, 6	28, 30	36.6 d
11		212.8 s			216.6 s
12	3.09 d (14.7) 2.75 d (14.7)	49.3 t	9, 11, 13		49.8 t
13		48.8 s			49.2 s
14		50.9 s			51.9 s
15	1.88 dd (7.6, 12.8) 1.68 br d (12.8)	46.3 t	14, 16, 30		46.7 t
16	4.90 t (7.6)	70.3 d	14, 15, 17, 20	18	71.5 d
17	2.93 d (7.6)	58.7 d	16, 18, 20, 21, 22	21	59.3 d
18	1.14 s	20.4 q	13, 17	8β, 16β	20.4 q
19	1.20 s	20.0 q	9, 8, 11	1β, 8β	20.3 q
20		80.1 s			80.8 s
21	1.57 s	25.4 q	17, 20, 22	17α, 26	25.5 q
22		216.1 s			217.2 s
23	2.23 m; 2.15 m	32.7 t	22, 24, 25		33.1 t
24	3.48 m; 3.29 m	38.5 t	22, 23, 25, 26, 27		38.1 t
25		69.1 s			70.8 s
26	1.36 s	30.1 q	24, 25	21	29.4 q
27	1.36 s	29.9 q	24, 25		29.2 q
28	1.48 s	24.6 q	3, 4, 5, 29	10α	28.2 q
29	1.09 s	22.1 q	3, 4, 5, 28	3β	26.1 q
30	1.44 s	18.9 q	8, 14	10α, 17α	19.8 q

[a] ^1H NMR in 400 MHz and ^{13}C NMR in 100 MHz in C_5D_5N, *J* in Hz in parentheses. ^{13}C NMR (CD_3OD) of **6** was reported in ref. [5].



1 **6**

Figure 1. Structures of compounds **1** and **6**.

of **6** (figure 1) except that **1** has one more carbonyl group on ring A than **6**. In the $^{1}H-^{1}H$ COSY spectrum, no correlation is observed between the δ4.25 (s) with other protons, which confirms carbons at δ 211.0 (s) and δ 81.1 (d) are assigned to be C-2 and C-3 bearing a hydroxyl substituent on ring A, respectively. In ROESY spectrum, correlations of 3β-H/1β-H and 3β-H/29β-H suggested the α-hydroxylation at C-3, which is identical with those of 3-hydroxyl-cucurbitacins isolated from *Picria fel-terrae* previously. Further evidence of the structure **1** is given by the detailed analysis of the key HMBC and ROESY correlations (table 1). On these grounds **1** is deduced to be 2,11,22-trioxo-3α,16α-dihydroxy-(20-*S*,25)-epoxycucurbit-5-ene.

This is the first report on the isolation of cucurbitacin with side chain containing (20*S*,25)-epoxy instead of (20*S*,24)-epoxy reported from *Picria fel-terrae* Lour. It is noticeable that there are very few examples of triterpenoids with side chain containing pyranyl ring [7], therefore, compound **1** might be considered one of the characteristic constituents of *Picria fel-terrae*.

The other four known isolated compounds have been identified by the spectral comparison with those of reference data. Thus **2–5** have been verified as picfeltarraegenin I (**2**) [8], picfeltarraenin IA (**3**) [9], picfeltarraenin IB (**4**) [9], and picfeltarraenin IV (**5**) [2], respectively.

3. Experimental

3.1 General experimental procedures

Melting points were determined on a XRC-1 micromelting point apparatus and are uncorrected. FAB-MS and HRFAB-MS were obtained on a Finnigan MAT 90 instrument using glycerol as the liquid matrix. 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 and detection was carried out by spraying with 10% H_2SO_4 ethanol followed by heating.

3.2 Plant material

The whole plant was collected in Wuzhou city, Guangxi province, China in 2001 and identified by Y.N. Zheng, the Testing Centre of Guilin Sanjin Pharm. Co., China, where a voucher specimen (PF-0101) is kept.

3.3 Extraction and isolation

Dried and powdered plant materials (10 kg) were 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 MeOH fraction was concentrated and subjected to chromatography 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 repeated CC on silica gel using $CHCl_3$/MeOH as eluent. This led to the isolation of compounds **1** (205 mg) and **2** (250 mg). Fraction VIII was subjected to repeated CC on silica gel. Elution with solvent $CHCl_3$/MeOH–H_2O yielded compounds **3** (10500 mg) and **4** (520 mg), respectively. Compound **5** (150 mg) was isolated by the same way from fraction IX with $CHCl_3$/MeOH/H_2O (3:1:0.1).

Picfeltarraenone II (**1**): colourless needles, mp 234–236°C; $[\alpha]_D^{26} + 34.3$ (*c* 0.20, MeOH); UV (MeOH) λ_{max} nm (log ε): 225 (3.73); IR (KBr) ν_{max} cm^{-1}: 3444 (OH), 1693 (C═O), 1633 (C═C); FAB-MS (glycerol) *m/z* 501 $[M + H]^+$, 485, 469. HRFAB-MS: *m/z* 501.3229 $[M + H]^+$ (calcd for $C_{30}H_{45}O_6$, 501.3216). ^1H NMR and ^{13}C NMR data: see table 1.

Purity analysis: Picfeltarraenin IA (20 mg) was dissolved in 2 mL MeOH, and 2, 4, 6, 8, and 10 μL of which were dotted on a Silica gel TLC plate, then developed with three kinds of solvent systems ($CHCl_3$/MeOH, 10:3; $CHCl_3$/MeOH–H_2O, 4:1:0.1; EtOAc/MeCOMe, 6:4), each sample exhibited single spot detected by spraying 10% H_2SO_4 ethanol followed by heating. The content of picfeltarraenin IA was determined on a Waters 515 HPLC (Waters 996 Photodiode Array Detector) using Phenomenex C_{18} (5 μm, 250 mm × 4.6 mm); mobile phase: MeOH/H_2O (70:30); detection wavelength: 263.9 nm; flow rate: 0.9 ml/min. The purity of picfeltarraenin IA (10.5 g) was determined to be 98.87%, which can be used as authentic sample for quality control, according to *Technical Requirements of Standard Compounds for the Quality Control of TCM* issued by SFDA.

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