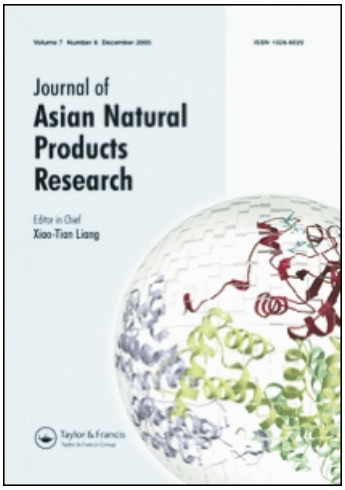

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Na Li[a]; Zhi-Da Min[a]; Hou-Ming Wu[b]
[a] Department of Natural Products Chemistry, China Pharmaceutical University, Nanjing, People's Republic of China [b] State Key Laboratory of Bio-organic and Natural Products Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, People's Republic of China

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NEW OLEANENE-TYPE TRITERPENE SAPONINS FROM *PUERARIA PEDUNCULARIS*

NA LI[a], ZHI-DA MIN[a,*] and HOU-MING WU[b]

[a]*Department of Natural Products Chemistry, China Pharmaceutical University, Nanjing 210009, People's Republic of China;* [b]*State Key Laboratory of Bio-organic and Natural Products Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China*

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Two new oleanane-type triterpene saponins named pedunsaponins B (**2**) and C (**3**) were isolated from the roots of *Pueraria peduncularis*. Their structures were determined to be 3-*O*-(6-*O*-methyl)-β-glucuronopyranosyl-3β,15α-dihydroxyolean-12-en-16-one (**2**), and 3-*O*-β-glucopyranosyl-(1 → 3)-β-glucuronopyranosyl-3β,15α-dihydroxy-oleana-12-en-16-one (**3**), on the basis of spectroscopic evidence.

Keywords: *Pueraria peduncularis*; Leguminosae; Triterpene saponins; Pedunsaponins B and C

INTRODUCTION

Pueraria peduncularis Grah. which grows in the southwest of the People's Republic of China is a plant of Leguminosae. It has been used occasionally as a substitute for *P. lobata* whose root is one of the most important oriental crude drugs as an antiperspirant, antipyretic, and antispasmodic agent. However, *P. peduncularis* is toxic and is usually used to kill fish and insects [1]. In order to use *P. lobata* more safely, we have distinguished them phytochemically. Isoflavones and flavones were the main constituents of *P. lobata* and seven triterpene sapogenols and nineteen triterpene saponins were also isolated from *P. lobata* and *P. thomsonii* in low quantity [2–6]. There are only scarce reports on the constituents of *P. peduncularis* [1].

In the preceding paper [7], we reported the isolation of a new triterpene saponin from *P. peduncularis* named pedunsaponin A (**1**), which possesses a new triterpene sapogenol: 3β,15α,23-trihydroxyoleana-12-en-16-one. Our continuing studies resulted in the isolation of two new oleanaene-type triterpene saponins: pedunsaponin B (**2**) and C (**3**). In this paper, the isolation and the structure elucidation of **2** and **3** are described.

*Corresponding author. Tel: +86-25-3220992. Fax: +86-25-3302827. E-mail: zhdmin32@hotmail.com

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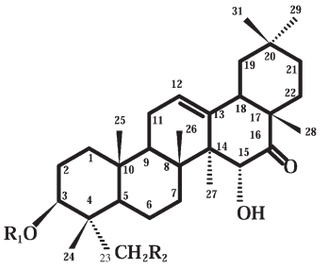
RESULTS AND DISCUSSION

The dried roots of *P. peduncularis* were extracted with 95% EtOH. The extract was dissolved in water and partitioned successively with $CHCl_3$ and *n*-BuOH. The *n*-BuOH extract was subjected to normal- and reversed-phase column chromatography to yield **2** and **3**.

Compound **2** was obtained as a colorless amorphous powder, $[\alpha]_D^{25}$ −13.5 (c 1.0, MeOH). The high resolution FAB-MS *m/z* 647.4205 $[M+H]^+$ gave a molecular formula of $C_{37}H_{58}O_9$ ($C_{37}H_{58}O_9$ requires 647.4202). The IR spectrum showed absorption bands at 1752 and 1701 cm^{-1} due to an ester and a carbonyl group and at 1627 cm^{-1} due to a double bond. The ^1H NMR spectrum showed the presence of an oleanene-type triterpene with eight methyl signals at δ 0.84 (3H, s), 0.87 (3H, s), 0.92 (3H, s), 1.01 (3H, s), 1.17 (3H, s), 1.20 (3H, s), 1.30 (3H, s), and 1.31(3H, s), and an olefinic proton signal at δ 5.48 (1H, s). The ^{13}C NMR spectrum displayed one anomeric carbon signal at δ 107.3.



	R_1	R_2
1	glc (1-3) glcA	OH
2	6-O-methyl- glcA	H
3	glc (1-3) glcA	H

Comparison of the ^{13}C NMR spectral data of the aglycon part of **2** with that of **1** (Table I) showed that the C-23 signal revealed a significant difference due to the absence of OH-23 in **2**. The upfield shift of the C-4 signal (−4.1 ppm) and downfield shifts of C-3 (+7.9 ppm), C-5 (+8.3 ppm) and C-24 (+2.0 ppm) of **2** were observed. Therefore, the aglycon of **2** could be assigned as 3β,15α-dihydroxyolean-12-en-16-one. In support of this structure, the HMBC experiment showed correlations between the protons of CH_3-23 and the C-24 (δ 15.8), C-3 (δ 89.0), C-4 (δ 39.5), and C-5 (δ 55.5) signals. The $^{13}C-^1H$ long-range correlation between the anomeric proton H-1′ (δ 4.99) of the sugar and C-3 (δ 89.0) of the aglycon indicated that the sugar should be attached at C-3 of the aglycon. With the aid of DQF-COSY the spectrum, the signals at δ 4.99, 4.09, 4.26, 4.48, 4.60 were assigned to H-1′, 2′, 3′, 4′, 5′, of the sugar. In the HMBC spectrum, H-5′ (δ 4.60) was correlated with the carboxyl group (δ 170.8) which was correlated with the methoxyl protons (δ 3.73). Based on this and the ROEs between H-1′, H-3′ and H-5′ in the ROESY spectrum, the sugar was deduced to be 6-*O*-methyl-β-glucuronopyranoside. From the above mentioned evidence, the structure of **2** was established as 3-*O*-(6-*O*-methyl)-β-glucuronopyranosyl-3β,15α-dihydroxyolean-12-en-16-one, named pedunsaponin B (Fig. 1).

Compound **3** was obtained as a colorless amorphous powder, $[\alpha]_D^{25}$ −7.5 (c 1.0, MeOH). The FAB-MS (negative-ion mode) showed ions at *m/z* 793 $[M-H]^-$, 631 $[M-H\text{-glc}]^-$. Its molecular formula, $C_{42}H_{66}O_{14}$ was determined by high resolution FAB-MS at *m/z*

TABLE I ^{13}C NMR spectral data of compounds **1–3***

Carbon	1	2	3
1	39.0	39.0	38.9
2	26.2	26.7	26.7
3	81.1	89.0	89.0
4	43.6	39.5	39.6
5	47.2	55.5	55.5
6	18.4	18.6	18.7
7	35.7	35.9	36.0
8	41.9	41.7	41.9
9	47.3	47.1	47.1
10	36.9	36.9	37.0
11	24.2	24.0	24.2
12	125.9	125.8	125.9
13	142.1	142.0	142.1
14	54.3	54.2	54.3
15	72.9	72.7	72.9
16	217.5	217.2	217.4
17	46.5	46.4	46.5
18	53.1	53.0	53.1
19	48.0	47.9	48.1
20	31.0	30.9	31.1
21	36.0	35.9	36.0
22	31.1	30.9	31.1
23	64.2	28.1	28.2
24	13.8	15.8	15.9
25	16.5	17.0	17.2
26	17.9	17.7	17.9
27	22.0	21.8	22.1
28	28.2	28.1	28.2
29	33.2	33.0	33.2
30	23.4	23.4	23.5
	Glucuronic acid		
1′	105.3	107.3	106.7
2′	74.2	75.5	74.4
3′	87.4	77.9	88.0
4′	71.6	73.2	72.1
5′	76.9	77.2	77.0
6′	173.4	170.8	174.0
OCH_3		52.0	
	Glucose		
1″	105.8		106.0
2″	75.6		75.6
3″	78.3		78.3
4″	71.9		71.7
5″	78.9		78.8
6″	62.5		62.6

* Measured in pyridine-d_5 at 150 MHz for **1** and **2** and at 100 MHz for **3**.

795.4546 $[M + H]^+$. The occurrence of eight methyl signals at δ 0.86 (3H, s), 0.89 (3H, s), 0.91 (3H, s), 1.00 (3H, s), 1.17 (3H, s) 1.20 (3H, s) 1.27 (3H, s), and 1.35 (3H, s) and an olefinic proton signal at δ 5.50 (1H, s) in the ^1H NMR spectrum suggested it to be an oleanene derivative. The anomeric carbon signals at δ 106.0 and 106.7 in the ^{13}C NMR spectrum indicated the existence of two sugar moieties in the molecule. The ^{13}C NMR signals for the aglycon part of **3** were in accordance with those of **2** (Table I) and the signals for the sugar part were in accordance with those of **1** (Table I). Therefore, **3** (pedunsaponin C) was concluded to be 3-*O*-β-glucopyranosyl-(1 → 3)-β-glucuronopyranosyl-3β,15α-dihydroxyolean-12-en-one.

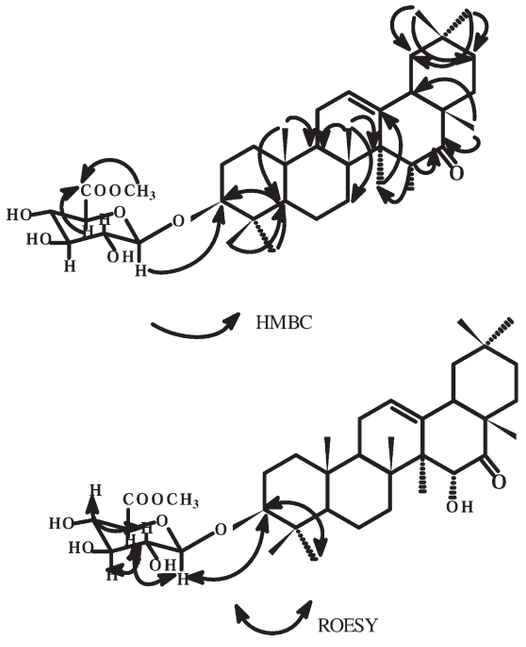


FIGURE 1 Selected ROESY and HMBC correlations of **2**.

EXPERIMENTAL SECTION

General Experimental Procedures

Optical rotations were determined on a Perkin–Elmer digital polarimeter. IR spectra were acquired with a Nicolet Impact-410 IR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were measured with Varian Inova-600 and Bruker ACF-400 NMR spectrometers. Mass spectra were acquired with Auto-Spec-Ultima-Tof and HP5989A mass spectrometers.

PLANT MATERIAL

The roots of *P. peduncularis* were collected in the Sichuan Province of the People's Republic of China, and identified by Dr Gouyue Zhong of China Pharmaceutical University. A voucher sample (No. 970816) is deposited in the herbarium of China Pharmaceutical University, Nanjing, China.

Extraction and Isolation

The dried roots (5 kg) of *P. peduncularis* were extracted with 95% EtOH three times under reflux. The resultant extract (340 g) was dissolved in water and partitioned successively with $CHCl_3$ and *n*-BuOH. The *n*-BuOH extract (250 g) was subjected to silica gel column chromatography eluting with $CHCl_3$–CH_3OH(5:1–1:1) to afford fractions 1–6. Fraction 4 was further separated by silica gel using $CHCl_3$–CH_3OH(5:1–1:1) and Sephadex LH-20 column chromatography using H_2O to provide **2** (10 mg). Fraction 6 was further separated by

silica gel eluting with $CHCl_3$–CH_3OH(3:1–1:1), Sephadex LH-20 with H_2O and ODS column chromatography with CH_3OH–H_2O (7:3) to afford **3** (5 mg).

Pedunsaponin B (**2**): colorless amorphous powder; $[\alpha]_D^{25}$ −13.5 (c 1.0, MeOH); IR (KBr) ν_{max} 3455, 2951, 1752, 1701, 1627, 1460, 1442, 1386, 1246, 1165, 1089, 1055, 1011, 982 cm^{-1}; ^1H NMR (600 MHz, Pyr-d_5) δ 5.48 (1H, s, H-12), 4.99 (1H, d, J = 7.8 Hz, H-1′), 4.79 (1H, s, H-15), 4.60 (1H, d, J = 10.2 Hz, H-5′), 4.48 (1H, t, J = 9.0 Hz, H-4′), 4.26 (1H, t, J = 9.0 Hz, H-3′), 4.09 (1H, t, J = 8.4 Hz, H-2′), 3.73 (3H, s, OCH_3), 3.38 (1H, dd, J_1 = 4.2 Hz, J_2 = 12.0 Hz, H-3), 2.58 (1H, dd, J_1 = 4.2 Hz, J_2 = 12.0 Hz, H-18), 1.31 (3H, s, H-27), 1.30 (3H, s, H-23), 1.20 (3H, s, H-28), 1.17 (3H, s, H-26), 1.01 (3H, s, H-24), 0.92 (3H, s, H-25), 0.87 (3H, s, H-30), 0.84 (3H, s, H-29), ^{13}C NMR spectral data see Table I; HRFAB-MS *m/z* 647.4205 $[M + H]^+$ (calcd. for $C_{37}H_{59}O_9$ 647.4202).

Pedunsaponin C (**3**): colorless amorphous powder; $[\alpha]_D^{25}$ −7.5 (c 1.0, MeOH); IR (KBr) ν_{max} 3439, 2949, 1701, 1614, 1460, 1386, 1328, 1158, 1078, 1031, 1012 cm^{-1}; ^1H NMR (600 MHz, Pyr-d_5) δ 5.50 (1H, s, H-12), 4.79 (1H, s, H-15), 3.36 δ 5.48 (1H, br, s, H-3), 2.59 (1H, br. d, J = 12.0 Hz, H-18), 1.35 (3H, s, H-27), 1.27 (3H, s, H-23), 1.20 (3H, s, H-28), 1.16 (3H, s, H-26), 1.00 (3H, s, H-24), 0.91 (3H, s, H-25), 0.88 (3H, s, H-30), 0.86 (3H, s, H-29); ^{13}C NMR spectral data see Table I; Negative FAB-MS *m/z* 793 $[M - H]^-$ (100), 631 (17); HRFAB-MS *m/z* 795.4546 $[M + H]^+$ (calcd. for $C_{42}H_{67}O_{14}$ 795.4541).

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