Two New Oleanene-Type Triterpenoid Saponins from *Pueraria peduncularis*

Na LI[1], Zhi Da MIN[1,*], Hou Ming WU[2]

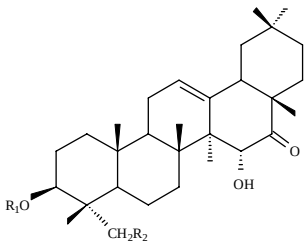
[1] Department of Natural Products Chemistry, China Pharmaceutical University, Nanjing 210009
[2] State Key Laboratory of Bio-organic and Natural Products Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032

Abstract: From the radix of *Pueraria peduncularis* Grah., two new oleanene-type triterpenoid saponins named pedunsaponins B (**2**) and C (**3**) were isolated. Their structures were determined as 3-O-(6-O-methyl)-β-D-glucuronopyranosyl-3β,15α-diol-12-oleanene-16-one (**2**) and 3-O-β-D-glucopyranosyl-(1→3)-β-D-glucuronopyranosyl-3β,15α-diol-12-oleanene-16-one (**3**) on the basis of spectroscopic evidence and chemical reactions.

Keywords: *Pueraria peduncularis*, Leguminosae, triterpenoid saponin.

Pueraria peduncularis Grah. (Leguminosae) is a plant growing in the southwest of China. The plants of *Pueraria* DC. are important oriental crude drugs used as a perspiration, antipyretic and antispasmodic agents. Various isoflavonoids and triterpenoid saponins[1,2,3,4,5] have been discovered from them. Since *P. peduncularis* is toxic, it has never been used as a source for medicines. There are only scarce reports on its chemical constituents.

In the preceding paper[6], we reported the isolation of a new triterpenoid saponin from *P. peduncularis* named pedunsaponin A (**1**), which possesses a new triterpenoid sapogenol: 3β,15α,23-triol-12-oleanene-16-one. Our continuing studies resulted in the isolation of two new triterpenoid saponins: pedunsaponins B (**2**) and C (**3**). This paper deals with the isolation and the structural elucidation of these two compounds.



	R_1	R_2
pedunsaponin A (1)	glc(1→3)glcA	OH
pedunsaponin B (2)	6-O-Me glcA	H
pedunsaponin C (3)	glc(1→3)glcA	H

Dried roots of *P. peduncularis* were extracted with 95% EtOH three times under reflux. The extract was dissolved in water and partitioned with $CHCl_3$ and n-BuOH. The n-BuOH layer was concentrated and subjected to normal and reversed phase column chromatography to yield **2** and **3**.

Pedunsaponin B (**2**) was obtained as a white amorphous powder. ESI-MS exhibited an ion peak at *m/z* 670 $[M+Na+H]^+$. Liebermann-Burchard Reaction and Molish Reaction were positive. The IR spectrum showed absorption band at 1752, 1701 cm^{-1} due to carbonyl group and at 1627 cm^{-1} due to double bond. The occurrence of eight methyl signals at δ 0.84 (s), 0.87 (s), 0.92 (s), 1.01 (s), 1.17 (s), 1.20 (s), 1.30 (s), 1.31 (s) and a proton signal at δ 5.48 in the ^1H NMR suggested it to be an oleanene derivative. The anomeric carbon signal at δ 107.3 in the ^{13}C NMR indicated the presence of one sugar moiety in its structure.

Comparison the ^{13}C NMR spectral data of the aglycone part of **2** with those of **1** (pedunsaponin A) (**Table 1**) suggested that only the signal of C-23 was significantly different due to the absence of 23-OH. The C-4 (δ 43.6) signal of **1** was downfield shifted compared to that of **2** (δ 39.5) due to β-effect of 23-OH, while the signals of C-5 (δ 47.2), C-3 (δ 81.1), C-24 (δ 13.8) of **1** were upfield shifted compared to those of **2** (δ 55.5, δ 89.0, δ 15.8) due to γ-effect of 23-OH. Therefore, the aglycone of **2** should be 3β,15α-diol-12-oleanene-16-one.

By the aid of DQF-COSY 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) correlated with the carboxyl group (δ 170.8) which in turn correlated with the methoxyl group (δ 3.73). So the sugar was 6-O-methyl β-D-glucuronopyranoside.

In the HMBC spectrum, the long range correlation between H-1 (δ 4.99) of the sugar and C-3 (δ 89.0) of the aglycone indicated that **2** was 3-O-(6-O-methyl)-β-D-glucuronopyranosyl-3β,15α-diol-12-oleanene-16-one, named pedunsaponin B.

Pedunsaponin C (**3**) was obtained as a white amorphous powder. FAB-MS showed ion peaks at *m/z* 794 $[M]^+$, 631 $[M\text{-glc}]^+$, 545 $[M\text{-glc-glcA}]^+$. Liebermann-Burchard Reaction and Molish Reaction were positive. The occurrence of eight methyl signals at δ 0.86 (s), 0.89 (s), 0.91 (s), 1.00 (s), 1.17 (s), 1.20 (s), 1.27 (s), 1.35 (s) and a proton signal at δ 5.50 in the ^1H NMR suggested it to be an oleanene derivative. The anomeric carbon signals at δ 106.0 and δ 106.7 in the ^{13}C NMR indicated the existence of two sugar moieties in its structure.

The ^{13}C NMR signals of the aglycone part of **3** were in accordance with those of **2** (**Table 1**) and the signals of the sugar part were consistent with those of **1** (**Table 2**). Therefore, **3** was concluded to be 3-O-β-D-glucopyranosyl-(1→3)-β-D-glucurono-pyranosyl-3β,15α-diol-12-oleanene-16-one, named pedunsaponin C.

Table 1. ^{13}C NMR spectral data for the aglycone of **1**, **2** and **3** (in Py-d_5)

C	**1**	**2**	**3**	C	**1**	**2**	**3**
1	39.0	39.0	38.9	16	217.5	217.2	217.4
2	26.2	26.7	26.7	17	46.5	46.4	46.5
3	81.1	89.0	89.0	18	53.1	53.0	53.1
4	43.6	39.5	39.6	19	48.0	47.9	48.1
5	47.2	55.5	55.5	20	31.0	30.9	31.1
6	18.4	18.6	18.7	21	36.0	35.9	36.0
7	35.7	35.9	36.0	22	31.1	30.9	31.1
8	41.9	41.7	41.9	23	64.2	28.1	28.2
9	47.3	47.1	47.1	24	13.8	15.8	15.9
10	36.9	36.9	37.0	25	16.5	17.0	17.2
11	24.2	24.0	24.2	26	17.9	17.7	17.9
12	125.9	125.8	125.9	27	22.0	21.8	22.1
13	142.1	142.0	142.1	28	28.2	28.1	28.2
14	54.3	54.2	54.3	29	33.2	33.0	33.2
15	72.9	72.7	72.9	30	23.4	23.4	23.5

Table 2. ^{13}C NMR spectral data for the sugar of **3** and **1** (in Py-d_5)

C	**3**	**1**	C	**3**	**1**
glc-1	106.0	105.8	glcA-1	106.7	105.3
glc-2	75.6	75.6	glcA-2	74.4	74.2
glc-3	78.3	78.3	glcA-3	88.0	87.4
glc-4	71.7	71.9	glcA-4	72.1	71.6
glc-5	78.8	78.9	glcA-5	77.0	76.9
glc-6	62.6	62.5	glcA-6	174.0	173.4

Table 3. ^{1}H NMR spectral data for **2** and **3** (in Py-d_5)

H	**2**	**3**
12	5.48	5.50
15	4.79	4.79
23	1.30	1.27
24	1.01	1.00
25	0.92	0.91
26	1.17	1.17
27	1.31	1.35
28	1.20	1.20

29	0.84	0.86
30	0.87	0.89

References

1. J. Kinjo, I. Miyamoto, K. Murakami, K. Kida, T. Tomimatsu, M. Yamasaki, T. Nohara, *Chem. Pharm. Bull.*, **1985**, *33*(3), 1293.
2. J. Kinjo, T. Takeshita, Y. Abe, N. Terada, H. Yamashita, M. Yamasaki, K. Takeuchi, K. Murakami, T. Tomimatsu, T. Nohara, *Chem. Pharm. Bull.*, **1988**, *36*(3), 1174.
3. T. Arao, J. Kinjo, T. Nohara, R. Isobe, *Chem. Pharm. Bull.*, **1995**, *43*(7), 1176.
4. T. Arao, T. Idzu, J. Kinjo, T. Nohara, R. Isobe, *Chem. Pharm. Bull.*, **1996**, *44*(10),1970.
5. T. Arao, J. Kinjo, T. Nohara, R. Isobe, *Chem. Pharm. Bull.*, **1997**, *45*(2), 362.
6. N. Li, R. Yang, Z. Min, H. Wu, *J. of China Pharmaceutical University*, **1999**, *30*(3), 166.

Received 21 December 1999