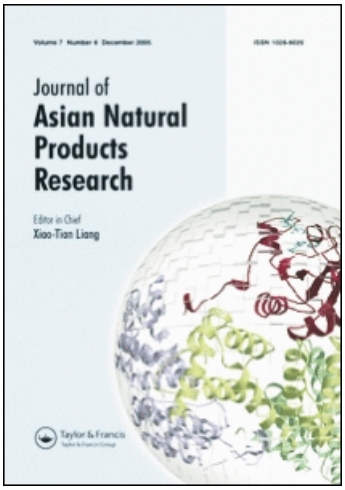

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Saikosaponin v-1 from Roots of *Bupleurum Chinense* DC

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SAIKOSAPONIN v-1 FROM ROOTS OF *BUPLEURUM CHINENSE* DC.

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Three triterpenoidal saponins, saikosaponin v-1(**1**), 6″-O-acetyl-saikosaponin b_2 (**2**) and 6″-O-acetyl-saikosaponin *d*(**3**) were isolated from the roots of the title plant and the structures were identified on the basis of spectral analysis. Saikosaponin v-1 is a new compound, which was identified as 3β,16α,23,28-tetrahydroxy-olean-11,13(18)-dien-30-oic acid–3-O-β-D-glucopyranosyl-(1 → 3)- β-D-fucopyranosyl-30-O-xylitol ester.

Keywords: *Bupleurum chinense* DC.; *Umbelliferae*; Saikosaponins; Acetylsaikosaponins; Saikosaponin v-1

INTRODUCTION

The roots of *Bupleurum chinense* DC. are well-known and very important in the prescriptions of Chinese Traditional Medicine. *B.chinense* and *B.scorzonerifolium* have been officially accepted and recorded in the Chinese Pharmacopoeia. Some saikosaponins from *Bupleurum* L. are considered as the major bioactive components, mainly used for their antiinflammatory, antihepatotoxic and immune activities [1]. *And using the measurement technique of enzyme secretion in pancreatic acini, we studied the promotion of the 95% EtOH extract from B. chinese on pancreatic exocrine. The result showed the extract cause significant increase of enzymes secretion.* Previously

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we reported the isolation and structural determination of the new saponins and a chromoside together with the some known compound from the 95% EtOH extract of B. chinese [2–6]. A further investigation of the plant provided three saikosaponins, saikosaponin v-1(**1**). 6″-O-acetyl-saikosaponin b_2 (**2**) and 6″-O-acetyl-saikosaponin *d* (**3**) from the roots of the plant. Saikosaponin v-1 is a new compound. Its structure was mainly elucidated to be 3β,16α,23,28-tetrahydroxy-olean-11,13(18)-dien-30-oic acid-3-O-β-D-glucopyranosyl-(1 → 3)-β-D-fucopyranosyl-30-O-xylitol ester by spectral analysis.

RESULTS AND DISCUSSION

A crude saponin was afforded from the plant by methods described in the Experimental. The crude saponin was separated by repeated chromatography and HPLC to give saponins **1–3**.

In the ^{13}C NMR spectra of compounds **2–3**, signals were found to be identical with those of the known compounds, 6″-O-acetyl-saikosaponin b_2 (**2**) and 6″-O-acetyl-saikosaponin *d* (**3**). **1** was obtained as white powder. A quasi-molecular ion was observed at *m/z* 967[M + Na]$^+$ in the TOF-MS. The ^{1}H NMR spectrum exhibited five angular methyl signals (δ 0.81, 0.90, 0.97, 1.45 and 1.63). Its UV spectrum showed absorption bands at 242, 251 and 261 nm, ^{1}H NMR showed two signals at 6.58 (1H, *d*, *J* = 10.0 Hz, H-11) and 5.65 (1H, *d*, *J* = 10.0 Hz, H-12), ^{13}C NMR exhibited 4 signals at 137.5,130.6,126.8 and 125.9 corresponding to C-13, 18,12 and 11, respectively. These data indicated that **1** had the skeleton of olean-11,13 (18)-diene. The ^{13}C NMR spectrum of **1** showed that the aglycone moiety possessed four hydroxyl groups at δ 81.6,67.5 (CHOH) and at δ 64.0,64.8 (CH_2OH) and a carbonyl group at δ 178.9, and the ^{13}C NMR data of the aglycone moiety were in good agreement with those of saikosaponin v [7]. Therefore, the structure of aglycone was identified as 3β,16α,23,28-tetrahydroxy-olean-11,13 (18)-dien-30-oic acid. Acidic hydrolysis of **1** on TLC gave fucose and glucose which were identical with authentic samples. The signals at δ 5.34 (1H, *d*, *J* = 8.0 Hz), 4.99 (1H, *d*, *J* = 8.0 Hz), 1.44 (3H, *d*, *J* = 7.0 Hz) in the ^{1}H NMR and δ 106.6, 106.0, 17.2 in the ^{13}C NMR spectrum (Tab. I) indicated that **1** was a diglycoside containing a fucose and a glucose with β-anomeric configuration. TOCSY data also supported the above speculation and showed that there was a third spin system with the lowest signal at δ 4.94. ^{13}C NMR and HMQC data suggested that the third spin system was a xylitol.

TABLE I ^{13}C NMR data of 1 (125 MHz, C_5D_5N)

	Aglycon			*Sugar*	
1	38.3	16	67.5	Fuc 1	105.9
2	26.1	17	45.3	2	71.8
3	81.6	18	130.6	3	85.2
4	43.6	19	31.7	4	72.2
5	47.3	20	44.2	5	71.0
6	18.1	21	30.7	6	17.2
7	32.2	22	23.7	Glc 1	106.6
8	41.0	23	64.0	2	75.8
9	53.9	24	13.1	3	78.4
10	36.4	25	18.8	4	71.5
11	126.8	26	17.2	5	78.7
12	125.9	27	21.7	6	62.6
13	137.5	28	64.8	Xylitol 1	67.5
14	41.9	29	20.9	2	72.2
15	33.4	30	178.9	3	74.0
				4	74.3
				5	64.0

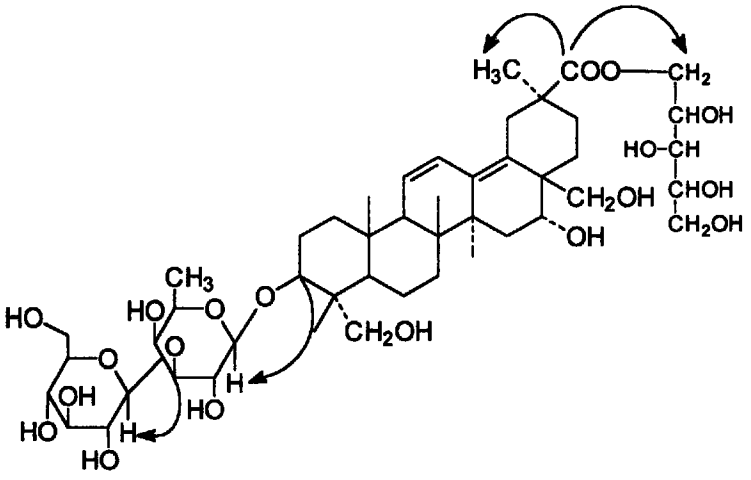

FIGURE 1 HMBC of saikosaponin v-1.

One and two-dimensional NMR techniques (^1H NMR, ^{13}C NMR, ^1H-^1H COSY, HMQC, TOCSY) permitted assignments of the proton and carbon signals of **1** (Tab. I). HMBC experiments showed that the anomeric proton of glucose (δ 5.34) was correlated with the carbon 3 of the fucose (δ 85.2), the anomeric proton of fucose (δ 4.99) was correlated with the carbon 3 of the aglycon (δ 81.5), the protons-1 of xylitol (δ 4.94) was correlated with the carbonyl group. The results provided unambiguous information about the positions of the glycosidic and ester linkage shown in Figure 1.

Thus **1** was elucidated as 3β,16α,23,28-tetrahydroxy-olean-11,13 (18)-diene-30-oic acid-3-O-β-D-glucopyranosyl-(1 → 3)- β-D-fucopyranosyl-30-O-xylitol ester. **1** was a new saponin named saikosaponin v-1.

EXPERIMENTAL SECTION

General Experimental Procedures

Melting points were measured with an X_4 micromelting point apparatus and are uncorrected. UV spectra were taken in MeOH on a Shimadzu UV 260 spectrometer. ^{1}H NMR, ^{13}C NMR, ^{1}H-^{1}H COSY, HMQC, TOCSY and HMBC spectra were recorded in pyridine-d_5 with a Bruker Am-500 instrument. MS spectrum were recorded on a MALDI-TOF MS instrument. For column chromatography silica gel (Marine Chemical Plant, Qing Dao) and Sephadex LH-20, RP-18 (Chemical Reagent Factory, Tian Jin) were used. TLC was performed on RP-18 precoated layer (Merck).

Plant Material

The roots of *Bupleurum chinense* DC. were collected in Baoji, Shaanxi Province of China and were identified by Prof. Li Shenghua and Dr. Chen Hubiao, Beijing Medical University. A voucher specimen has been deposited in the herbarium of the Department of Natural Medicines, Beijing Medical University.

Extraction and Isolation

The powered roots of the plant (13.5 kg) were extracted with 95% EtOH at room temp. The extract was concentrated under reduced pressure and diluted with H_2O. The aqueous solution was extracted with EtOAc and *n*-BuOH respectively. *n*-BuOH extract (170.0 g) was chromatographed on silica gel column to give Frs 1–17. Fr.1(7.2 g) was subjected to repeated chromatography on silica gel column eluted with EtOAc–EtOH–H_2O (50 : 2 : 1) and on Sephadex LH-20 column eluted with MeOH to give compound **2** (30.0 mg), **3** (10.0 mg). Fr.17 was subjected to repeated chromatography on silica gel chromatography eluted with $CHCl_3$–MeOH–H_2O (65 : 35 : 10), Sephadex LH-20 column eluted with MeOH and on HPLC eluted with 46% MeOH to give compound **1** (25.5 mg).

Identification

Compound 1 white powder, UV λ_{max}^{MeOH} nm: 242, 251, 261. ^{1}H NMR (C_5D_5N) δ: 0.81, 0.90, 0.97, 1.44, 1.63 (each 3H, *s*, 5 × CH_3), 6.58 (1H, *d*, J = 10.5 Hz, H-12), 5.65 (1H, *d*, J = 10.5 Hz, H-11), 5.34 (1H, *d*, J = 8.0 Hz, glucose H-1), 4.99 (1H, *d*, J = 8.0 Hz, fucose H-1), 1.44 (3H, *d*, J = 7.0 Hz, fucose CH_3), 5.34 (1H, *dd*, J = 11.0, 2.5 Hz, xylitol H-1), 4.94 (1H, *dd*, J = 11.0, 8.0 Hz, xylitol H-1). ^{13}C NMR (C_5D_5N) data see Table I.

Compound 2 white powder, UV λ_{max}^{MeOH} nm: 242, 251, 261. ^{1}H NMR (C_5D_5N) δ: 0.88, 0.91, 0.98, 1.00, 1.04, 1.67 (each 3H, *s*, 6 × CH_3), 6.70 (1H, *d*, J = 10.5 Hz, H-12), 5.72 (1H, *dd*, J = 10.5, 3 Hz, H-11), 5.25 (1H, *d*, J = 8.0 Hz, glucose H-1), 5.02 (1H, *d*, J = 8.0 Hz, fucose H-1), 1.51 (3H, *d*, J = 6.2 Hz, fucose CH_3), 1.94 (3H, *s*, CH_3CO). ^{13}C NMR (C_5D_5N) (aglycone No.1–30; Fuc.1–6; Glc.1–6; CH_3CO) δ: 38.5, 26.1, 81.8, 43.7, 47.5, 18.3, 32.0, 41.1, 54.0, 36.5, 126.2, 126.2, 136.1, 41.9, 32.4, 67.8, 45.3, 133.1, 39.1, 32.5, 35.5, 24.5, 64.2, 13.1, 18.8, 17.3, 21.9, 64.8, 25.1, 32.4; 106.0, 71.5, 85.4, 71.5, 71.0, 17.3; 106.4, 75.3, 78.1, 72.1, 75.5, 64.8; 170.8, 20.7. The above data are agreement with those of 6″-O-acetyl-saikosaponin b_2 [8].

Compound 3 white powder, UV λ_{max}^{MeOH} nm: 242, 251, 261. ^{1}H NMR (C_5D_5N) δ: 0.88, 0.91, 0.98, 1.00, 1.04, 1.67 (each 3H, *s*, 6 × CH_3), 6.03 (1H, *d*, J = 10.5 Hz, H-12), 5.69 (1H, *dd*, J = 10.5, 3 Hz, H-11), 5.34 (1H, *d*, J = 8.0 Hz, glucose H-1), 4.95 (1H, *d*, J = 8.0 Hz, fucose H-1), 1.42 (3H, *d*, J = 6.2 Hz, fucose CH_3), 1.93 (3H, *s*, CH_3CO). ^{13}C NMR (C_5D_5N) (aglycone No.1–30; Fuc.1–6; Glc.1–6; CH_3CO) δ:38.7, 26.1, 81.9, 43.7, 47.5, 17.7, 31.9, 41.9, 53.1, 36.4, 131.2, 131.2, 84.9, 43.8, 35.5, 77.2, 45.4, 51.4, 38.5, 31.6, 36.8, 31.3, 64.8, 13.0, 18.9, 19.3, 18.1, 77.8, 33.8, 24.5; 106.0, 71.9, 85.4, 71.9, 71.1, 17.3; 106.4, 75.5, 78.1, 72.1, 75.3, 64.5; 170.8, 20.8. The above data are agreement with those of 6″-O-acetyl-saikosaponin *d* [8].

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