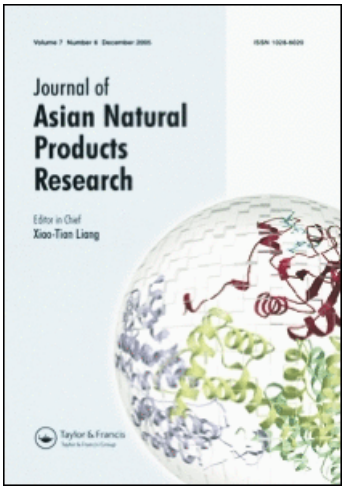

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Triterpenoid saponins from the rhizome of *Polygonatum sibiricum*

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ORIGINAL ARTICLE

Triterpenoid saponins from the rhizome of *Polygonatum sibiricum*

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Three new triterpenoid saponins, polygonoides C (**1**), D (**2**), and E (**3**), were obtained from the ethanolic extract of the rhizome of *Polygonatum sibiricum* Redoute. On the basis of NMR and ESI-MS spectra, and chemical evidence, the structures of the three new compounds were elucidated as 3-*O*-α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranosyl-(1 → 4)-β-D-glucopyranosyl-3β,7β,22β-trihydroxy-oleanolic acid (**1**), 3-*O*-α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranosyl-(1 → 4)-β-D-glucopyranosyl-3β,7β,22β-trihydroxy-oleanolic acid methyl ester (**2**), and 3-*O*-β-D-glucopyranosyl-(1 → 3)-β-D-glucopyranosyl-(1 → 4)-[α-L-rhamno-pyranosyl-(1 → 2)]-β-D-glucopyranosyl-3β,21β-dihydroxy-oleanolic acid 28-*O*-β-D-glucopyranosyl-(1 → 3)-β-D-glucopyranosyl-(1 → 3)-β-D-glucopyranoside (**3**).

Keywords: *Polygonatum sibiricum*; triterpenoid saponins; polygonoide C; polygonoide D; polygonoide E

1. Introduction

Polygonatum sibiricum, widely distributed in China, is a perennial herbaceous plant belonging to the family of Liliaceae. *P. sibiricum*, especially its root or stem, has been used as a medicine for more than 2000 years and as foodstuff as well. It is capable of lowering blood glucose and lipid levels, regulating and enhancing the immune system, and preventing aging [1]. In addition, *P. sibiricum* has been explored as health care cosmetics of pure Chinese medicine such as masks, cleansing milk, conditioner, and toothpaste.

In recent years, many compounds such as alkaloids [2], polysaccharides [3], steroidals, and triterpenoid saponins [4,5] have been isolated from *P. sibiricum*. Since triterpenoid saponins possess anti-inflammatory [6], antibacterial [7], antifungal [8], anti-angiogenic [9], and antiproliferative activities [10], attempts have been made to isolate them from a variety of herbal plants [7–10]. In order to preserve the natural resource, other groups have even tried to synthesize them [11,12]. However, until now reports on terpenoid saponins isolated from *P. sibiricum* are still limited [5,13]. It was believed that there are a relatively large amount of ursane-type and oleanane-type terpenoid saponins in *P. sibiricum.* Aiming to seek for potentially bioactive and novel compounds, we isolated three new oleanane-type terpenoid saponins from the rhizome of *P. sibiricum.* Their structures were elucidated on the basis of NMR and ESI-MS spectra and chemical evidence.

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2. Results and discussion

The EtOH extract of the fresh rhizome of *P. sibiricum* was concentrated and partitioned further into petroleum ether and H_2O soluble fractions. The H_2O phase was successively separated on the macroporous adsorption resin AB-8, reversed-phase silica gel ODS and MCI, and furnished three oleanane-type triterpenoid saponins (**1–3**).

Compound **1** was obtained as a white amorphous powder and reacted positively with the Ehrlich reagent. Its molecular formula was determined as $C_{48}H_{78}O_{19}$ by HR-ESI-MS at *m/z* 957.5051 $[M - H]^-$.

In the ^{1}H NMR spectrum (shown in Table 1), there were seven methyl singlets at δ 0.74, 0.80, 0.84, 0.88, 0.92, 1.03, and 1.13, respectively, one methyl doublet at δ 1.11 (d, $J = 8.0$ Hz), one olefinic proton at δ 5.16 (br s), and three anomeric protons of sugar at δ 5.61 (d, $J = 5.1$ Hz), 4.84 (d, $J = 7.9$ Hz), and 4.78 (d, $J = 7.9$ Hz), respectively. The ^{13}C NMR (shown in Table 2) and ^{135}DEPT spectra revealed 48 carbon signals, of which 18 were assigned to the sugar moieties and 30 to the aglycone moiety. The positive results of the Ehrlich reagent and the fact that the aglycone moiety contained 30 carbons indicated that compound **1** was a triterpenoid saponin. Because of the carbon signals at δ 172.9 for the carbonyl group, δ 121.6 and δ 144.1 for the double bond, this compound was identified as an oleanane type [14,15].

Different from the oleanolic acid, compound **1** had only eight methylene signals at δ 23.3, 25.5, 25.5, 26.9, 28.0, 38.2, 41.2, and 47.1, respectively. However, oleanane-type saponin contains 10 methylene carbon signals, which indicates the existence of two oxygen-containing substituent groups. Considering three carbon signals at δ 68.0, 74.3, and 91.3, there should be three oxygen-bearing carbons, among which C-3 (δ 91.3) was the oxygen-bearing carbon connected to the sugar. The carbon signals at δ 68.0 and 74.3 indicated the possible substitution by the hydroxyl groups. For the E ring, the chemical shift of C-21 (δ 41.2) moved towards downfield, indicating that C-22 might be substituted by the hydroxyl group. In the HMBC spectrum, there were correlations between H-21 (δ 2.14) and C-22 (δ 74.3), which confirmed that C-22 bore a hydroxyl group. Proton signals at 3.72 (dd, $J = 11.8$, 4.2 Hz) [16–18] provided the evidence for the β-configuration of the hydroxyl group at C-22. For the B ring, there were no methylene signals for C-6 (δ 18) and C-7 (δ 33) commonly observed for oleanolic acid, while there was only one methylene signal at δ 25.5, indicating the substitution by the hydroxyl group at C-7 which caused the downfield shift of C-6. In the HMBC spectrum, the correlations between H-6 (δ 2.26) and C-7 (δ 68.0) proved that a hydroxyl group was attached to C-7. The orientation of the hydroxyl group at C-7 was determined to be β-configuration by the $^3J_{H7.H6}$ value (8.9 Hz).

For the study of the sugar moiety, **1** was hydrolyzed to obtain sapogenin and sugar. After the acetylation of the sugar, the products were determined to be glucose and rhamnose with the content ratio of 2:1 using gas chromatography coupled with mass spectrometry (GC–MS). It was inferred that the sugar moiety of **1** was composed of two glucose and one rhamnose residue. From the ^{1}H NMR spectrum, three anomeric protons of sugars could be seen, which further proved the existence of three sugars. Since the value of $J_{1,2}$ was 7.9 Hz, the configurations of both glucoses were β while the configuration was α for rhamnose ($J = 5.1$ Hz). The bonding position of the sugar moiety was confirmed by the HMBC experiment (Figure 1). Strong HMBC correlations were observed between Glc-1-H-1 at δ 4.78 and C-3 of sapogenin at δ 91.3, Glc-2-H-1 at δ 4.84, and C-4 of Glc-1 at δ 76.9, which indicated that glucose 1 was connected to C-3 of sapogenin while

Table 1. ^{1}H NMR (500 MHz) spectroscopic data of compounds **1–3** (in pyridine-d_5, J in Hz).

1		**2**		**3**	
1	1.72 (m)	1	1.72 (m)	1	1.76 (m)
2	1.84 (m), 1.68 (m)	2	1.84 (m), 1.67 (m)	2	1.84 (m), 1.68 (m)
3	3.22 (m)	3	3.24 (m)	3	3.73 (m)
5	1.75 (m)	5	1.76 (m)	5	1.50 (m)
6	2.26 (d, $J = 8.9$), 1.58 (m)	6	2.24 (d, $J = 8.9$), 1.58 (m)	6	1.54 (m), 0.98 (m)
7	3.72 (m)	7	3.71 (m)	7	1.69 (m), 1.11 (m)
9	1.72 (m)	9	1.73 (m)	9	1.67 (dd, $J = 14, 6.6$)
11	1.96 (m)	11	1.98 (m)	11	1.97 (m)
12	5.16 (br s)	12	5.15 (br s)	12	5.83 (br s)
15	1.71 (m)	15	1.74 (m)	15	1.71 (m)
16	1.81 (m)	16	1.85 (m)	16	1.82 (m)
18	2.71 (m)	18	2.73 (m)	18	2.76 (m)
19	2.65 (m), 1.34 (m)	19	2.65 (t, $J = 13.3$), 1.34 (m)	19	2.68 (t, $J = 14.0$), 1.34 (m)
21	2.14, 1.62 (m)	21	2.14, 1.62 (m)	21	3.84 (dd, $J = 12.0, 4.4$)
22	3.72 (dd, $J = 11.8, 4.2$)	22	3.72 (dd, $J = 11.8, 4.2$)	22	2.53, 1.62 (m)
23	0.92 (s)	23	0.95 (s)	23	0.97 (s)
24	0.88 (s)	24	0.87 (s)	24	0.91 (s)
25	0.80 (s)	25	0.79 (s)	25	0.84 (s)
26	0.74 (s)	26	0.73 (s)	26	0.81 (s)
27	1.03 (s)	27	1.04 (s)	27	1.16 (s)
29	0.84 (s)	29	0.83 (s)	29	0.89 (s)
30	1.13 (s)	30	1.13 (s)	30	1.23 (s)
–	Glc-1-H-1 4.78 (d, $J = 7.9$)	–	Glc-1-H-1 4.75 (d, $J = 8.0$)	–	Glc-1-H-1 4.73 (d, $J = 6.8$)
–	Glc-2-H-1 4.84 (d, $J = 7.9$)	–	Glc-2-H-1 4.95 (d, $J = 7.8$)	–	Glc-2-H-1 4.86 (d, $J = 6.8$)
–	Rha-H-1 5.61 (d, $J = 5.1$)	–	Rha-H-1 5.63 (d, $J = 5.1$)	–	Glc-3-H-1 5.41 (d, $J = 6.9$)
–	H-6 1.11 (d, $J = 8.0$)	–	H-6 1.12 (d, $J = 8.0$)	–	Glc-1′-H-1 4.62 (d, $J = 7.2$)
–	–	–	OCH_3 3.70 (s)	–	Glc-2′-H-1 4.92 (d, $J = 7.2$)
–	–	–	–	–	Glc-3′-H-1 5.06 (d, $J = 7.2$)
–	–	–	–	–	Rha-H-1 5.62 (d, $J = 5.1$)
–	–	–	–	–	H-6 1.83 (d, $J = 5.8$)

Table 2. ^{13}C NMR (125 MHz) spectroscopic data of compounds **1–3** (in pyridine-d_5).

Aglycone	**1**	**2**	**3**	Sugar	**1**	**2**	**3**	Sugar	**3**
1	38.2	38.2	38.9	Glc-1	–	–	–	Glc-1′	–
2	25.5	25.5	27.1	1	101.9	101.9	103.3	1	93.2
3	91.3	91.2	91.0	2	74.0	74.0	79.2	2	76.9
4	38.9	38.9	39.6	3	75.2	75.2	76.1	3	84.4
5	56.3	56.2	56.5	4	76.9	76.8	81.2	4	71.8
6	25.5	25.5	19.0	5	74.6	74.6	77.9	5	78.7
7	68.0	68.0	33.2	6	61.9	61.8	62.7	6	64.0
8	42.6	42.6	40.5	Glc-2	–	–	–	Glc-2′	–
9	48.0	48.0	48.0	1	105.2	105.2	106.2	1	107.0
10	36.6	36.7	37.1	2	79.5	79.5	75.6	2	76.8
11	23.3	23.3	24.5	3	76.3	76.4	85.3	3	85.0
12	121.6	121.6	123.0	4	70.5	70.5	69.7	4	71.6
13	144.1	144.2	144.6	5	75.7	75.6	78.3	5	78.4
14	41.6	41.7	42.2	6	63.8	63.8	62.7	6	67.7
15	28.0	28.0	28.1	Rha	–	–	–	Glc-3′	–
16	26.9	26.9	26.7	1	102.3	102.3	104.5	1	108.7
17	44.0	44.0	44.1	2	70.5	70.5	71.0	2	76.1
18	45.6	45.5	44.7	3	72.3	72.4	72.5	3	78.8
19	47.1	47.0	47.6	4	74.2	74.3	73.3	4	71.3
20	31.0	31.1	36.7	5	69.2	69.2	70.1	5	78.8
21	41.2	41.2	73.2	6	19.1	19.0	19.2	6	67.6
22	74.3	74.2	38.8	Glc-3	–	–	–	–	–
23	28.3	28.4	27.2	1	–	–	106.8	–	–
24	17.2	17.2	16.0	2	–	–	74.8	–	–
25	16.0	16.0	16.1	3	–	–	78.2	–	–
26	21.3	21.3	21.6	4	–	–	70.7	–	–
27	25.9	25.9	23.4	5	–	–	78.1	–	–
28	172.9	173.3	177.2	6	–	–	63.0	–	–
29	32.7	32.7	31.8	–	–	–	–	–	–
30	22.4	22.4	23.3	–	–	–	–	–	–
OCH_3	–	51.5	–	–	–	–	–	–	–

glucose 2 was connected to C-4 of glucose 1. At the same time, the HMBC spectrum showed that there was a correlation peak between Rha-H-1 of rhamnose at δ 5.61 and C-2 of glucose 2 at δ 79.5. Thus, it could be concluded that rhamnose was connected to C-2 of glucose 2.

Accordingly, the structure of compound **1** was elucidated as 3-*O*-α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranosyl-(1 → 4)-β-D-glucopyranosyl-3β,7β,22β-trihydroxy-oleanolic acid, named polygonoide C.

Compound **2** was obtained as a white amorphous powder, giving a positive coloration with the Ehrlich reagent. The HR-ESI-MS showed an $[M - H]^-$ ion peak at *m/z* 971.5222, corresponding to the molecular formula $C_{49}H_{80}O_{19}$.

The ^1H NMR and ^{13}C NMR spectra of compound **2** were similar to those of compound **1**, except for the presence of the methoxyl group at δ_H 3.70 and δ_C 51.5 in **2**. The HMBC correlation between the proton at δ_H 3.70 and the carbonyl carbon at δ_C 173.3 (C-28) indicated that the methoxyl group was connected to the carbonyl carbon [14] (Figure 1). Thus, compound **2** could be determined as the methyl ester of **1**, i.e. 3-*O*-α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranosyl-(1 → 4)-β-D-glucopyranosyl-3β,7β,22β-trihydroxy-oleanolic acid methyl ester, named polygonoide D.

Compound **3** was obtained as a white amorphous powder and turned gel-like

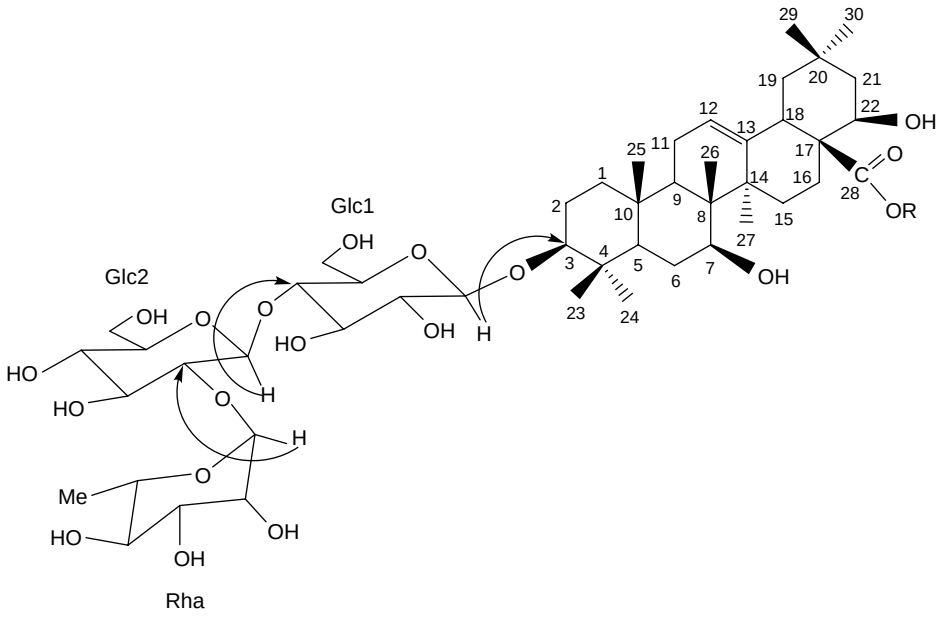

Figure 1. The structures and key HMBC correlations of compounds **1** and **2**, respectively. R = H in **1** and CH_3 in **2**.

when containing a small amount of water. It also gave positive results for the Ehrlich reagent. The HR-ESI-MS showed an $[M - H]^-$ ion peak at *m/z* 1589.7235, corresponding to the molecular formula $C_{72}H_{118}O_{38}$.

In the ^{1}H NMR spectrum, there were seven methyl signals ranging from δ 0.81 to 1.23 of sapogenin, while another methyl signal at δ 1.83 was assigned to the rhamnose. There were eight protons with chemical shifts at δ 4.62, 4.73, 4.86, 4.92, 5.06, 5.41, 5.62, and 5.83 respectively, among which the proton at δ 5.83 was assigned to H-12 and the other seven signals to the anomeric protons of sugars.

In the ^{13}C NMR spectrum, there were 72 carbon signals, among which 42 were assigned to the sugar moieties and 30 to the aglycone moiety. Based on the positive result of the Ehrlich reagent and the fact that the aglycone moiety contained 30 carbons, compound **3** was triterpenoid saponin as well. Because of the carbon signals at δ 177.2 for the carbonyl group, δ 123.0 and δ 144.6 for the double bond, this compound was also an oleanane type. In the ^{135}DEPT spectrum, there were only nine carbon signals of methylenes for the aglycone moiety, indicating the existence of one oxygen-containing substituent group. The carbon signals of A, B, C, and D rings in compound **3** were almost identical to those of oleanolic acid, with the exception of the E ring. The chemical shift of C-20 in **3** shifted towards downfield about 5 ppm, C-22 about 6 ppm, and C-21 about 40 ppm [14,15], suggesting the existence of the hydroxyl group at C-21. Proton signals at 3.84 (dd, J = 12.0, 4.4 Hz) suggested that the configuration of the hydroxyl group should be β [16,18]. Thus, the sapogenin moiety in **3** should be 3β,21β-dihydroxy-oleanolic acid.

For the study of the sugar moiety, **3** was hydrolyzed to obtain the sapogenin and the sugar. After the acetylation of the sugar, the products were determined to be glucose and rhamnose with the content ratio of 6:1 using GC–MS. It was inferred that the sugar moiety of **3** was composed of six glucose

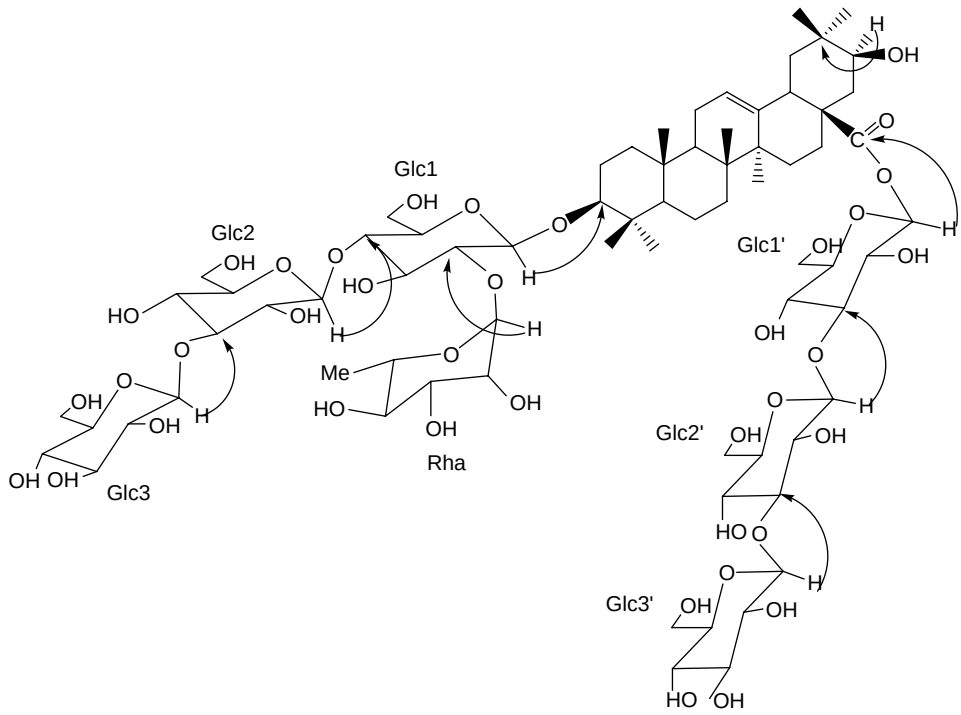

Figure 2. The structure and key HMBC correlations of compound **3**.

and one rhamnose residue. In the ^{1}H NMR spectrum, the *J* values of anomeric protons of glucose were 6.8–7.2 Hz indicating the β configuration, while the configuration was α for rhamnose ($J = 5.1$ Hz).

In the ^{13}C NMR spectrum, there were seven anomeric carbon signals at δ 108.7, 107.0, 106.8, 106.2, 104.5, 103.3, and 93.2, respectively. The connection mode of sugars can be determined by 2D NMR spectra.

The anomeric carbon signal at δ 93.2 showed the existence of the ester glycosidic bond. In the HMBC spectrum, the cross-peak between Glc-1′-H-1 at δ 4.62 and the carbonyl carbon at δ 177.2 (C-28) indicated that glucose 1′ was attached to the C-28 of sapogenin by the ester bond. The anomeric proton Glc-2′-H-1 at δ 4.92 showed HMBC correlations with the C-3 at δ 84.4 of glucose 1′, indicating that glucose 2′ was attached to the C-3 of glucose 1′. The HMBC correlations from Glc-3′-H-1 at δ 5.06 to Glc-2′-C-3 at δ 85.0 indicated that glucose 3′ was attached to the C-3 of glucose 2′ (Figure 2).

In the HMBC spectrum, the cross-peak between Glc-1-H-1 at δ 4.73 and the oxygen-bearing carbon at δ 91.0 indicated that glucose 1 was attached to the C-3 of the sapogenin. The HMBC correlation between the Glc-2-H-1 at δ 4.86 and the Glc-1-C-4 at δ 81.2 indicated that glucose 2 was attached to the C-4 of glucose 1. At the same time, the correlation between the Rha-H-1 at δ 5.62 and the Glc-1-C-2 at δ 79.2 indicated that rhamnose was attached to the C-2 of glucose 1. The HMBC correlation between the Glc-3-H-1 at δ 5.41 and the Glc-2-C-3 at δ 85.3 indicated that glucose 3 was attached to the C-3 of glucose 2. Thus, the structure of **3** was elucidated as 3-*O*-β-D-glucopyranosyl-(1 → 3)-β-D-glucopyranosyl-(1 → 4)-[α-L-rhamnopyranosyl-(1 → 2)]-β-D-glucopyranosyl-3β,21β-dihydroxy-oleanolic

acid 28-*O*-β-D-glucopyranosyl-(1 → 3)-β-D-glucopyranosyl-(1 → 3)-β-D-glucopyranoside, named polygonoide E.

3. Experimental

3.1 General experimental procedures

Melting points were determined with an X4 micro-melting point apparatus and are uncorrected. The $[\alpha]_D$ values were obtained in MeOH at 20°C on a Perkin-Elmer 341 digital polarimeter. HR-ESI-MS were recorded on a Micromass UK Ltd spectrometer. NMR spectra were recorded in pyridine-d_5 with a Bruker Avance 500 NMR spectrometer, using TMS as the internal standard.

Macroporous adsorption resin AB-8 (30–40 μm; Chemical Plant of Nankai University, Tianjin, China), Sephadex LH-20 (20–80 μm; Pharmacia Fine Chemical Co. Ltd, Uppsala, Sweden), Cosmosil ODS (40–80 μm; Nacalai Tosoh Inc., Uetikon, Switzerland), and MCI gel CHP20P (75–150 μm; Mitsubishi Kasei Co., Tokyo, Japan) were used for column chromatography. $HSGF_{254}$ (precoated plate, Qingdao Haiyang Chemical Co., Qingdao, China) was used for thin layer chromatography.

3.2 Plant material

The rhizomes of *P. sibiricum* Redoute were collected from Xi'an, Shanxi Province of China in September 2007. The plant material was identified by Prof. Jingxiang Yang (Institute of Botany North-West, Chinese Academy of Science). The voucher specimen has been deposited in the herbarium of the Institute of Botany North-West, Chinese Academy of Science.

3.3 Extraction and isolation

Fresh rhizoma (25 kg) of *P. sibiricum* was extracted three times for 2 h, each time with 20% ethanol (v/v) at 60°C. The material to liquid ratio was 1:5 (kg/l). The ethanol extracts were evaporated under reduced pressure to give a residue (15 liters). The concentrated liquid was extracted using petroleum ether until the phase of petroleum ether turned colorless. The residual phase was separated by macroporous adsorption resin AB-8 (80 mm × 1500 mm) after concentration, and eluted by deionized water and ethanol with different concentrations. Fraction A eluted by 10% ethanol and fraction B eluted by 30% ethanol were collected. After concentration, fraction A was eluted on a MCI column by deionized water, 10% ethanol, and 20% ethanol in sequence. The eluent of 10% ethanol was concentrated and eluted again on an ODS column by deionized water and ethanol with different concentrations. The eluent of 10–15% ethanol was concentrated, followed by separation and purification on the ODS column repeatedly. After characterization by thin layer chromatograph (TLC), compound **3** (67 mg) was obtained.

Fraction B was concentrated and eluted by deionized water and 10–50% ethanol on the MCI column. The eluent of 30% ethanol was collected. It was then concentrated and eluted again on the ODS column by deionized water and ethanol with different concentrations. The eluent of 30–40% ethanol was collected. After concentration, it was separated and purified repeatedly on the ODS column. After characterization by TLC, 103 mg of compound **1** and 52 mg of **2** were obtained.

3.3.1 Polygonoide C (*1*)

A white amorphous powder, mp 236–238°C, $[\alpha]_D^{20} + 31.0$ (MeOH, $c = 0.71$). ^{1}H NMR and ^{13}C NMR spectral data are shown in Tables 1 and 2, respectively. HR-ESI-MS *m/z:* 957.5051 $[M - H]^-$ (calcd for $C_{48}H_{77}O_{19}$, 957.5059).

3.3.2 Polygonoide D (*2*)

A white amorphous powder, mp 241–243°C, $[\alpha]_D^{20} + 33.0$ (MeOH, $c = 0.70$). ^{1}H NMR and ^{13}C NMR spectral data are shown in Tables 1 and 2, respectively.

HR-ESI-MS *m/z*: 971.5222 $[M - H]^-$ (calcd for $C_{49}H_{79}O_{19}$, 971.5216).

3.3.3 Polygonoide E (*3*)

A white amorphous powder and turned gel-like when containing a small amount of water, mp 257–259°C, $[\alpha]_D^{20} + 34.0$ (MeOH, $c = 0.81$). ^{1}H NMR and ^{13}C NMR spectral data are shown in Tables 1 and 2, respectively. HR-ESI-MS *m/z*: 1589.7235 $[M - H]^-$ (calcd for $C_{72}H_{117}O_{38}$, 1589.7223).

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