Five New Triterpene Saponins from *Pulsatilla patens* var. *multifida*

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Five new oleanane-type glycosides (**1**−**5**), along with two known triterpene saponins, were isolated from the roots of *Pulsatilla patens* var. *multifida* (Ranunculaceae). The structures of the new triterpene saponins were elucidated as 3-*O*-*β*-D-glucopyranosyl(1→2)-*β*-D-galactopyranosyl hederagenin 28-*O*-*β*-D-glucopyranosyl ester (**1**), hederagenin 3-*O*-[*β*-D-glucopyranosyl(1→2)][*β*-D-glucopyranosyl(1→6)]-*β*-D-galactopyranoside (**2**), 3-*O*-*β*-D-glucopyranosyl bayogenin 28-*O*-α-L-rhamnopyranosyl(1→4)-*β*-D-glucopyranosyl(1→6)-*β*-D-glucopyranosyl ester (**3**), 3-*O*-*β*-D-glucopyranosyl(1→2)-*β*-D-galactopyranosyl oleanolic acid 28-*O*-α-L-rhamnopyranosyl(1→4)-*β*-D-glucopyranosyl(1→6)-*β*-D-glucopyranosyl ester (**4**), and 3-*O*-[*β*-D-glucopyranosyl(1→2)][*β*-D-glucopyranosyl(1→6)]-*β*-D-galactopyranosyl hederagenin 28-*O*-α-L-rhamnopyranosyl-(1→4)-*β*-D-glucopyranosyl(1→6)-*β*-D-glucopyranosyl ester (**5**). Structure elucidation was accomplished by 1D and 2D NMR (HMQC, HMBC, and ROESY) methods, FABMS, and hydrolysis.

The roots of several *Pulsatilla* species (Ranunculaceae) are used for "blood-cooling" and detoxifying effects in traditional Chinese medicine.[1] A number of *Pulsatilla* species, such as *P. ambigua*, *P. chinensis*, *P. dahurica*, *P. koreana*, and *P. turczaninovii*, are employed in treating diarrhea, vaginal trichromoniasis, and bacterial infections, and pharmacological investigations have suggested that the triterpene saponins are important bioactive components.[2−6] We have previously reported on the isolation and structural elucidation of new triterpene glycosides such as pulsatillosides A and B from *P. chinensis* [5] and patensin from *P. patens* var. *multifida*.[6] Further investigation of the latter plant has now led to the purification of additional saponin constituents. In this paper we describe the isolation of seven saponins, the structures of which were determined with the aid of 1D and 2D NMR (^{13}C, ^{1}H, HMQC, HMBC, and ROESY) techniques, FABMS, and hydrolysis. An extensive search of the literature [7−11] indicated that compounds **1**−**5** are new structures.

Results and Discussion

The dried roots of *P. patens* var. *multifida* were extracted with MeOH. The MeOH extract was defatted with chloroform and subjected to column chromatography on D101 resin to afford saponin-rich fractions. These fractions were further separated on reversed-phase C_{18} columns to yield seven compounds. Compounds **1**−**5** (Chart 1) were found to be new saponins, whereas the remaining two isolates were identified as bayogenin 3-*O*-*β*-D-glucopyranoside and hederagenin 3-*O*-*β*-D-glucopyranosyl(1→2)-α-L-arabinopyranoside by comparison of their NMR data and physical properties with literature values.[4,12,13] Acid hydrolysis of the known compounds confirmed the identities of the aglycon and the sugar residues. The ^{1}H and ^{13} C NMR results (Tables 2 and 3) indicated an *β* configuration at the anomeric position of the glucose and galactose residues, and an α configuration for the rhamnose residue. The absolute configurations of these sugar residues were assumed to be D for glucose and galactose and L for rhamnose, consistent with the stereochemistry of naturally occurring monosaccharides.

Table 1. ^{13}C NMR Data of the Aglycon Moieties of Compounds **1**−**5**[a]

carbon	1	2	3	4	5
1	38.7	38.8	44.1	38.4	38.6
2	25.9	26.2	70.5	26.2	25.9
3	**82.8**	**83.0**	**83.0**	**88.5**	**82.9**
4	43.4	43.6	42.7	39.1	43.3
5	48.1	48.2	48.5	55.4	48.1
6	18.2	18.4	18.0	18.1	18.1
7	32.5	33.0	32.8	32.7	32.3
8	39.9	39.8	40.0	39.5	39.7
9	48.1	48.2	47.7	47.6	47.9
10	36.8	37.0	36.9	36.5	36.7
11	23.8	23.9	23.9	23.3	23.7
12	122.8	122.5	123.5	122.5	122.9
13	144.1	145.1	144.1	143.7	143.9
14	42.1	42.2	42.4	41.7	41.9
15	28.2	28.4	28.2	27.8	28.1
16	23.3	23.8	23.3	23.0	23.2
17	46.9	46.9	47.0	46.6	46.8
18	41.7	42.1	41.7	41.3	41.5
19	46.1	46.7	46.1	45.8	46.0
20	30.7	31.1	30.7	30.3	30.5
21	33.9	34.3	33.9	33.6	33.8
22	32.7	33.4	32.5	32.1	32.6
23	65.2	65.1	65.4	27.8	65.1
24	13.4	13.5	15.0	16.4	13.2
25	16.1	16.1	17.3	15.2	16.0
26	17.5	17.6	17.6	17.1	17.4
27	26.0	26.3	26.1	25.7	25.9
28	**176.4**	180.4	**176.5**	**176.1**	**176.4**
29	33.0	33.4	33.1	32.7	32.9
30	23.6	23.9	23.6	23.4	23.5

[a] Spectra were measured in pyridine-d_5. Assignments were established by interpretation of the ^{13}C DEPT, HMQC, and HMBC spectra. Values given in boldface indicate the glycosidic positions of the aglycon.

The FABMS of **1** showed a quasimolecular ion $[M + Na]^+$ at *m*/*z* 981, consistent with a molecular formula of $C_{48}H_{78}O_{19}$. Acid hydrolysis of **1** afforded hederagenin, which was identified by comparison with published spectral data,[14] and glucose and galactose, which were confirmed by high-performance TLC (HPTLC). Upon alkaline hydrolysis with 5 N NH_4OH, **1** yielded a prosapogenin and a sugar. The

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Chart 1

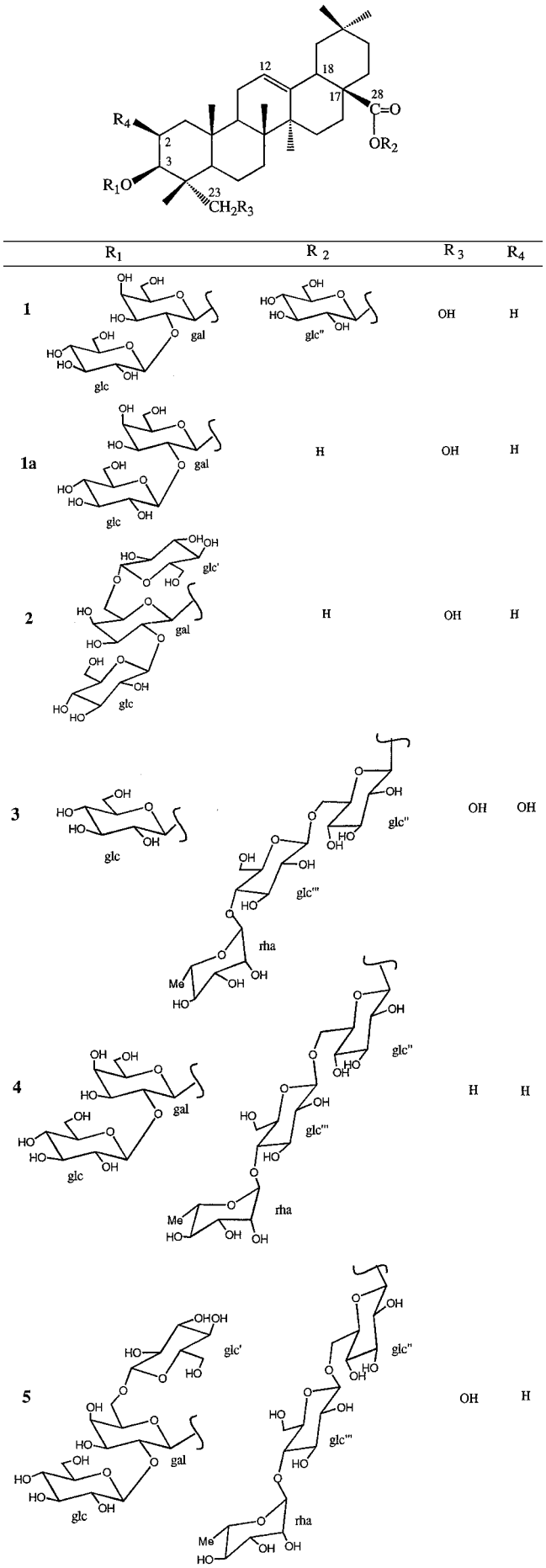

Table 2. ^{13}C NMR Data of the Saccharide Moieties of Compounds **1**−**5**[a]

carbon		**1**	**2**	**3**	**4**	**5**
			(a) For C-3			
gal	1	104.1	104.4		104.4	104.0
	2	**82.4**	**81.9**		**81.4**	**82.1**
	3	75.5	75.3		75.0	75.1
	4	69.8	69.6		69.5	69.3
	5	76.4	74.4		76.1	74.2
	6	62.3	**69.3**		62.2	**69.1**
glc	1	105.9	105.8	105.7	105.6	105.8
	2	76.6	76.6	75.5	76.5	76.4
	3	78.1	78.3	78.6	77.9	78.0
	4	71.1	71.4	71.6	71.2	71.1
	5	78.1	78.3	78.3	77.8	77.9
	6	62.1	62.7	62.6	61.8	62.5
glc′	1		105.0			104.9
	2		75.1			74.9
	3		78.5			78.3
	4		71.8			71.5
	5		78.4			78.2
	6		62.6			62.2
			(b) For C-28			
glc″	1	95.6		95.6	95.2	95.4
	2	74.1		73.9	73.5	73.7
	3	78.8		78.7	78.2	78.5
	4	71.0		70.9	70.4	70.6
	5	79.2		78.0	77.6	77.8
	6	62.0		**69.2**	**68.7**	**68.9**
glc‴	1			104.8	105.0	104.6
	2			75.3	74.9	75.1
	3			76.5	76.1	76.3
	4			**78.3**	**77.6**	**78.1**
	5			77.1	76.7	76.9
	6			61.3	60.9	61.1
rha	1			102.7	102.3	102.5
	2			72.5	72.1	72.3
	3			72.7	72.3	72.6
	4			74.0	73.4	73.8
	5			70.3	69.9	70.1
	6			18.5	18.1	18.3

[a] Recorded in pyridine-d_5. Assignments were established by ^{13}C DEPT, HMQC, and HMBC spectra. Values given in boldface indicate the interglycosidic positions of the sugar chain.

prosapogenin was identified as pulsatilloside D (**1a**) by comparison of NMR data and physical properties with literature values,[15] and the sugar was shown to be glucose by HPTLC. The ^{1}H and ^{13}C NMR spectra (Tables 1−3) of **1** suggested the presence of three sugar residues, clearly indicated by three anomeric carbon signals at δ 104.1, 105.9, and 95.6, and three anomeric proton signals at δ 5.01 (d, J = 7.8 Hz), 5.26 (d, J = 7.3 Hz), and 6.29 (d, J = 7.8 Hz). Thus, there was one glucose residue to be assigned on the aglycon besides the two sugar residues present at the C-3 position of the prosapogenin (**1a**). On the basis of the observation of a carbonyl signal at δ 176.4 (C-28) in the ^{13}C NMR spectrum, as well as an H-18 signal at δ 3.15 (br d, J = 9.8 Hz) in the ^{1}H NMR spectrum, it was concluded that the C-28 carboxyl group was glycosylated. Indeed, the HMBC spectrum of **1** revealed a cross-peak between the anomeric proton (H-1″) of glucose at δ 6.29 and the C-28 carbonyl carbon at δ 176.4. This led to the assignment of a glucose residue at the C-28 position of the aglycon. Compound **1** was thus a new triterpene glycoside whose structure was elucidated as 3-*O*-β-D-glucopyranosyl-(1→2)-β-D-galactopyranosyl hederagenin 28-*O*-β-D-glucopyranosyl ester.

The FABMS of compound **2** displayed a quasi-molecular ion peak at m/z 981 $[M + Na]^+$, suggesting the same molecular formula as **1**. Acid hydrolysis of **2** yielded hederagenin, glucose, and galactose. The ^{13}C and DEPT

Table 3. ^{1}H NMR Data of the Saccharide Moieties of Compounds **1**−**5**[a,b]

proton		1	2	3	4	5
			(a) For C-3			
gal	1	5.01 d (7.8)	5.00 d (7.8)		4.99 d (7.8)	4.99 d (7.8)
	2	4.59 dd (7.8, 8.6)	4.58 dd (7.8, 8.5)		4.57 dd (7.8, 8.6)	4.57 dd (7.8, 8.6)
	3	4.13[c]	4.06[c]		4.04[c]	4.05[c]
	4	4.52 m	4.39 m		4.40 m	4.39 m
	5	3.94 m	4.02 m		4.02 m	4.01 m
	6a	4.36[c]	4.29[c]		4.28[c]	4.28[c]
	6b	4.41[c]	4.64[c]		4.64[c]	4.63[c]
glc	1	5.26 d (7.3)	5.27 d (7.3)	5.15 d (7.7)	5.23 d (7.3)	5.23 d (7.3)
	2	4.11 dd (7.3, 9.0)	4.10[c]	4.02 dd (7.7, 9.0)	4.10 dd (7.3, 9.0)	4.09 dd (7.3, 9.0)
	3	4.15[c]	4.14 t (9.0)	4.14[c]	4.15[c]	4.14[c]
	4	4.26[c]	4.26 t (9.0)	4.21[c]	4.23[c]	4.23[c]
	5	3.74 m	3.74 m	3.88 m	3.74 m	3.72 m
	6a	4.33[c]	4.32[c]	4.32[c]	4.32[c]	4.31[c]
	6b	4.41[c]	4.44[c]	4.45[c]	4.49 [c]	4.49[c]
glc′	1		4.95 d (7.3)			4.95 d (7.3)
	2		3.99 dd (7.3, 9.1)			4.00 dd (7.3, 9.1)
	3		4.18 t (9.1)			4.19[c]
	4		4.22 t (9.1)			4.24[c]
	5		3.89 m			3.90 m
	6a		4.38[c]			4.38[c]
	6b		4.47[c]			4.46[c]
			(b) For C-28			
glc″	1	6.29 d (7.8)		6.21 d (8.1)	6.20 d (7.8)	6.20 d (7.8)
	2	4.18 dd (7.8, 9.0)		4.08 t (8.1)	4.10 dd (7.8, 8.9)	4.10 dd (7.8, 9.0)
	3	4.28 t (9.0)		4.18[c]	4.23[c]	4.24 [c]
	4	4.34[c]		4.27[c]	4.07[c]	4.32[c]
	5	4.01 m		4.07 m	4.06 m	4.07 m
	6a	4.44[c]		4.31[c]	4.28[c]	4.28[c]
	6b	4.46[c]		4.65[c]	4.63[c]	4.62[c]
glc‴	1			4.96 d (7.7)	4.96 d (7.8)	4.96 d (7.8)
	2			3.92 t (7.7, 9.0)	3.93 dd (7.8, 9.0)	3.92 dd (7.8, 9.0)
	3			4.13 t (9.0)	4.12 t (9.0)	4.12 t (9.0)
	4			4.39 t (9.0)	4.37 t (9.0)	4.37 t (9.0)
	5			3.65 m	3.63 m	3.62 m
	6a			4.06[c]	4.05[c]	4.06[c]
	6b			4.18[c]	4.18[c]	4.18[c]
rha	1			5.84 brs	5.82 brs	5.82 brs
	2			4.65[c]	4.66[c]	4.66[c]
	3			4.53[c]	4.53[c]	4.54[c]
	4			4.30[c]	4.33[c]	4.32[c]
	5			4.95[c]	4.93[c]	4.93[c]
	6			1.68 d (6.2)	1.67 d (5.9)	1.67 d (5.9)

[a] Recorded in pyridine-d_5. Assignments were established by HMQC, HMBC, and ROESY spectra. [b] *J* values (in Hz) in parentheses. [c] Overlapped signals.

NMR spectra of **2** displayed 48 signals, of which 30 were assigned to a triterpene moiety and 18 to the saccharide portion. Analysis of the NMR data of **2** and comparison with those of **1a** indicated that the former was different from the latter through the addition of a terminal glucopyranosyl residue. Further comparison of the ^{13}C NMR data (Table 2) of the saccharide portion revealed that one of three CH_2OH groups due to the glucose and galactose units showed a significant downfield shift (δ 69.3), suggesting that one of the C-6 CH_2OH groups of glucose or galactose was glycosylated.[16] Thus, a glucopyranosyl residue must be attached to the C-6 position of another glucose or galactose residue. Comparison of the ^{13}C NMR data of **2** with those of **1a** indicated further glycosylation shifts at C-6 (+7.0 ppm) and C-5 (−2.2 ppm) of the galactose moiety. Therefore, it was concluded that C-6 of the galactose was glycosylated. Furthermore, in the HMBC spectrum of **2**, correlation peaks were observed between H-1 (δ 5.00) of galactose and C-3 (δ 83.0) of the aglycon, between H-1 (δ 5.27) of glucose and C-2 (δ 81.9) of galactose, as well as between H-1′ (δ 4.95) of glucose and C-6 (δ 69.3) of galactose. These findings led to the assignment of **2** as hederagenin 3-*O*-[β-D-glucopyranosyl(1→2)][β-D-glucopyranosyl(1→6)]-β-D-galactopyranoside.

The FABMS of **3** displayed a $[M + Na]^+$ peak at *m*/*z* 1143, consistent with a molecular formula of $C_{54}H_{88}O_{24}$. The ^{1}H and ^{13}C NMR spectra suggested the presence of a triterpene possessing an olefinic bond, an ester carbonyl group, six methyl and one hydroxymethyl groups. An examination of the ^{1}H,^{1}H COSY spectrum rapidly established that C-2 and C-3 of the aglycon were both substituted by oxygen atoms [δ 4.80 (H-2), 4.30 (H-3)]. Acid hydrolysis of **3** afforded bayogenin, identified by comparison of the NMR data with literature values, [17] and glucose and rhamnose. A comparison of the ^{13}C NMR data of **3** with those of bayogenin indicated that the triterpene was glycosylated at C-3 and C-28. The ^{1}H and ^{13}C NMR spectra of **3** displayed signals for four sugar residues. Alkaline hydrolysis with 5 N NH_4OH afforded the known prosapogenin, bayogenin 3-*O*-β-D-glucopyranoside, identified by comparison with an authentic sample and literature values.[12] Accordingly, a glucose was attached to the C-3 position and a sugar chain composed of three residues could be assigned to the C-28 position of the aglycon. The interglycosidic linkages of the sugar chain were subsequently deduced from an HMBC experiment. Thus, the HMBC spectrum of **3** exhibited correlation peaks between H-1 (δ 5.15) of glucose and C-3 (δ 83.0) of the aglycon,

between H-1″ (δ 6.21) of the inner glucose and C-28 (δ 176.5), as well as between H-1‴ (δ 4.96) of the central glucose and C-6″ (δ 69.2) of the inner glucose. Moreover, the HMBC spectrum revealed a correlation cross-peak between H-1 (δ 5.84) of the terminal rhamnose and C-4‴ (δ 78.3) of the central glucose. All available evidence suggested that **3** was a new saponin whose structure could be deduced as 3-*O*-*β*-D-glucopyranosyl bayogenin 28-*O*-α-L-rhamnopyranosyl(1→4)-*β*-D-glucopyranosyl(1→6)-*β*-D-glucopyranosyl ester.

The FABMS of **4** showed a $[M + Na]^+$ ion at *m*/*z* 1273, consistent with a molecular formula of $C_{60}H_{98}O_{27}$. Comparison of the NMR spectral data of **4** with those of **1**−**3** showed a difference in the aglycon portion. The most significant feature of the ^1H NMR spectrum of **4** was the presence of seven methyl singlets in addition to a doublet due to the rhamnose residue. The aglycon of **4** was then identified as oleanolic acid [18] and confirmed by acidic hydrolysis. The ^1H and ^{13}C NMR spectra (Tables 1−3) of **4** revealed the presence of five sugar residues. The carbon signals at δ 88.5 (C-3) and at δ 176.1 (C-28) further suggested that both positions were glycosylated. Careful analysis of the NMR data revealed that the compound had the same glycosidic chains at C-3 and C-28 positions as in **1** and **3**, respectively. The HMBC and ROESY experiments also supported the above observation. Thus, the HMBC spectrum of **4** exhibited correlation signals between H-1 (δ 4.99) of galactose and C-3 (δ 88.5) of the aglycon, as well as between H-1 (δ 5.23) of glucose and C-2 (δ 81.4) of galactose. Moreover, correlations were also demonstrated between H-1″ (δ 6.20) of the inner glucose and C-28 (δ 176.1), between H-1‴ (δ 4.96) of the central glucose and C-6″ (δ 68.7) of the inner glucose, as well as between H-1 (δ 5.82) of the rhamnose and C-4‴ (δ 77.6) of the central glucose. Further information was derived from the results of an ROESY experiment. The ROESY spectrum revealed correlation peaks between H-1 of glucose (δ 5.23) and H-2 of galactose (δ 4.54), as well as between H-1 of rhamnose (δ 5.82) and H-4‴ of the central glucose (δ 4.37). All the available evidence led to the conclusion that **4** had the structure of 3-*O*-*β*-D-glucopyranosyl(1→2)-*β*-D-galactopyranosyl oleanolic acid 28-*O*-α-L-rhamnopyranosyl(1→4)-*β*-D-glucopyranosyl(1→ 6)-*β*-D-glucopyranosyl ester.

The FABMS of **5** displayed a quasimolecular ion $[M + Na]^+$ at *m*/*z* 1451, consistent with a molecular formula of $C_{66}H_{108}O_{33}$. The ^{13}C and DEPT NMR spectra of **5** contained 66 signals, of which 36 belonged to the saccharide portion and 30 to the triterpene aglycon. Acid hydrolysis of **5** afforded hederagenin, glucose, galactose, and rhamnose. Further comparison of ^{13}C NMR data for the saccharide portions indicated that **5** had the same glycosidic chains at C-3 and C-28 positions as **2** and **4**, respectively. Upon alkaline hydrolysis with 5 N NH_4OH, **5** yielded a prosapogenin which was identical with **2** by direct comparison of NMR data. The oligosaccharide structure was confirmed by 2D NMR. Thus, in the HMBC spectrum of **5**, correlation cross-peaks between H-1 (δ 5.23) of glucose and C-2 (δ 82.1) of galactose, between H-1′ (δ 4.95) of glucose and C-6 (δ 69.1) of galactose, between H-1‴ (δ 4.96) of the central glucose and C-6″ (δ 69.0) of the inner glucose, as well as between H-1 (δ 5.82) of rhamnose and C-4‴ (δ 78.1) of the central glucose were displayed. Hence, the structure of **5** was established as 3-*O*-[*β*-D-glucopyranosyl(1→2)][*β*-D-glucopyranosyl(1→6)]-*β*-D-galactopyranosyl hederagenin 28-*O*-α-L-rhamnopyranosyl(1→4)-*β*-D-glucopyranosyl(1→6)-*β*-D-glucopyranosyl ester.

Experimental Section

General Experimental Procedures. Optical rotations were measured on a Perkin-Elmer 241 polarimeter using a sodium lamp operating at 589 nm in MeOH. ^1H NMR (600, 500, or 400 MHz), ^{13}C NMR(150, 125 or 100 MHz), and 2D NMR spectra were determined on Varian Unity INOVA-600, −500 and JEOL JNM-EX 400 spectrometers. Fast-atom bombardment mass spectra (FABMS) were recorded in NBA matrix in the positive ion mode on a Finnigan MAT TSQ 7000 spectrometer. Column chromatography was carried out with ODS (10−40 μm, Merck). TLC was conducted on silica gel 60 F_{254} and RP-18 F_{254} S plates (Merck).

Plant Material. The roots of *P. patens* var. *multifida* (Pritz.) S. H. Li et Y. H. Huang were collected at Chifun, the Inner Mongolia Autonomous Region of China in May 1994, and authenticated by Dr. Xian-Min Cui. A voucher specimen has been deposited in the Herbarium of China Pharmaceutical University.

Extraction and Isolation. Dried roots of *P. patens* var. *multifida* (800 g) were extracted with MeOH (1500 mL × 3, 2 h each). The extracts were combined, evaporated, dissolved in H_2O and defatted with $CHCl_3$ (H_2O−$CHCl_3$, 1:1). The defatted extract was partitioned with *n*-BuOH and the *n*-BuOH layer was evaporated to dryness. The dark brown residue was redissolved in a small amount of MeOH and subjected to column chromatography on D101 resin (ca. 1000 g) using EtOH−H_2O as eluant. Fractions were collected and checked by TLC ($CHCl_3$−MeOH−H_2O, 6.5:3.5:1, lower layer).

Fractions 8−11 (2.2 g) containing a mixture of saponins **3**−**5** were separated using a reversed-phase C_{18} column (ca. 100 g, 10−40 μm) eluted with MeOH−H_2O (30:70−45:55) to yield pure compounds **5** (105 mg), **4** (60 mg), and **3** (200 mg). Fractions 20−24 (1.6 g) containing a mixture of **1**, **2** and two known triterpene glycosides were separated by column chromatography eluted with MeOH−H_2O (40:60 → 60:40) to yield pure compounds **1** (85 mg), **2** (50 mg), bayogenin 3-*O*-*β*-D-glucopyranoside (**6**, 40 mg) and hederagenin 3-*O*-*β*-D-glucopyranosyl(1→2)-α-L-arabinopyranoside (**7**, 70 mg).

Acid Hydrolysis of 1−5. Solutions of compounds (10 mg each) in 5% HCl−EtOH (5 mL) were heated in a boiling water bath for 8 h. The reaction mixture was diluted with H_2O and neutralized with Ag_2CO_3. The neutralized solution was extracted with EtOAc. The EtOAc layer was evaporated and chromatographed on Sephadex LH-20 using MeOH as eluant to yield the aglycon. The aglycon was analyzed by mmp, IR, and NMR and compared with an authentic sample. The H_2O layers were analyzed by HPTLC (*n*-BuOH−HOAc−H_2O, 4:1:1) to reveal the presence of glucose, galactose, rhamnose, or arabinose.

Alkaline Hydrolysis of 1−5. Each compound (30 mg) was refluxed with 5 N NH_4OH in 50% EtOH (10 mL) for 15 h. After cooling, the reaction mixture was neutralized with 2N HCl and extracted with *n*-BuOH. The *n*-BuOH layer was evaporated to dryness to give a residue, which was chromatographed on a C_{18} column (10−40 μm) eluted with MeOH−H_2O to yield the prosapogenin. The prosapogenins were identified by NMR spectra and/or by direct comparison with authentic samples.

Compound 1: Amorphous powder; mp 239−241 °C; $[\alpha]_{20}^{D}$ +20.8° (*c* 0.19, MeOH); IR ν_{max} (KBr) 3400 (OH), 1730 (COOR), 1640 (C=C) cm^{-1}; ^1H NMR (500 MHz, pyridine-d_5) δ 5.42 (1H, brs, H-12), 4.35 (1H, overlapped, H-23a), 4.13 (1H, overlapped, H-3), 3.73 (1H, overlapped, H-23b), 3.15 (1H, brd, J = 9.8 Hz, H-18), 1.17 (3H, s, Me), 1.09 (3H, s, Me), 1.06 (3H, s, Me), 0.90 (3H, s, Me), 0.86 (3H, s, Me), 0.85 (3H, s, Me); ^1H NMR data of the saccharide residues, see Table 3; ^{13}C NMR (125 MHz, pyridine-d_5), see Tables 1 and 2; FABMS *m*/*z* 981 $[M + Na]^+$.

Compound 2: Amorphous powder; mp 208−212 °C; $[\alpha]_{20}^{D}$ +21.2° (*c* 0.15, MeOH); IR ν_{max} (KBr) 3410 (OH), 1697 (COOH), 1630 (C=C) cm^{-1}; ^1H NMR (400 MHz, pyridine-d_5) δ 5.44 (1H, brs, H-12), 4.36 (1H, overlapped, H-23a), 4.15 (1H, overlapped, H-3), 3.74 (1H, overlapped, H-23b), 3.26 (1H, brd, J = 9.7 Hz, H-18), 1.20 (3H, s, Me), 1.06 (3H, s, Me), 0.98 (3H, s, Me), 0.92 (3H, s, Me), 0.92 (3H, s, Me), 0.90 (3H, s, Me); ^1H NMR data

of the saccharide residues, see Table 3; ^{13}C NMR (100 MHz, pyridine-d_5), see Tables 1 and 2; FABMS *m*/*z* 981 $[M + Na]^+$.

Compound 3: Amorphous powder; mp 228−232 °C; $[\alpha]_{20}^{D}$ −0.82° (*c* 0.12, MeOH); IR ν_{max} (KBr) 3405 (OH), 1740 (COOR), 1640 (C=C) cm^{-1}; ^{1}H NMR (600 MHz, pyridine-d_5) δ 5.39 (1H, brs, H-12), 4.32 (1H, overlapped, H-23a), 4.30 (1H, overlapped, H-3), 3.65 (1H, d, J = 11.4 Hz, H-23b), 3.14 (1H, brd, J = 9.9 Hz, H-18), 1.56 (3H, s, Me), 1.35 (3H, s, Me), 1.17 (3H, s, Me), 1.13 (3H, s, Me), 0.84 (3H, s, Me), 0.83 (3H, s, Me); ^{1}H NMR data of the saccharide residues, see Table 3; ^{13}C NMR (150 MHz, pyridine-d_5), see Tables 1 and 2; FABMS *m*/*z* 1143 $[M + Na]^+$.

Compound 4: Amorphous powder; mp 221−223 °C; $[\alpha]_{20}^{D}$ −8.4° (*c* 0.20, MeOH); IR ν_{max} (KBr) 3400 (OH), 1730 (COOR), 1636 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, pyridine-d_5) δ 5.39 (1H, brs, H-12), 4.16 (1H, overlapped, H-3), 3.13 (1H, brd, J = 9.8 Hz, H-18), 1.26 (3H, s, Me), 1.22 (3H, s, Me), 1.08 (3H, s, Me), 1.06 (3H, s, Me), 0.86 (6H, s, 2 × Me), 0.84 (3H, s, Me); ^{1}H NMR data of the saccharide residues, see Table 3; ^{13}C NMR (100 MHz, pyridine-d_5), see Tables 1 and 2; FABMS *m*/*z* 1273 $[M + Na]^+$.

Compound 5: Amorphous powder; mp 234−237 °C; $[\alpha]_{20}^{D}$ −10.2° (*c* 0.22, MeOH); IR ν_{max} (KBr) 3420 (OH), 1735 (COOR), 1640 (C=C) cm^{-1}; ^{1}H NMR (500 MHz, pyridine-d_5) δ 5.36 (1H, brs, H-12), 4.32 (1H, overlapped, H-23a), 4.10 (1H, overlapped, H-3), 3.71 (1H, overlapped, H-23b), 3.15 (1H, brd, J = 9.8 Hz, H-18), 1.13 (3H, s, Me), 1.08 (6H, s, 2 × Me), 0.94 (3H, s, Me), 0.86 (6H, s, 2 × Me); ^{1}H NMR data of the saccharide residues, see Table 3; ^{13}C NMR (125 MHz, pyridine-d_5), see Tables 1 and 2; FABMS *m*/*z* 1451 $[M + Na]^+$.

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