Five New Triterpenoid Saponins from the Roots of *Platycodon grandiflorum*

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Five new triterpenoid saponins, platycoside H [3-*O*-*β*-D-glucopyranosyl-(1→6)-*β*-D-glucopyranosyl-2*β*,3*β*,16*α*,23-tetrahydroxyolean-12-en-28-oic acid 28-*O*-*β*-D-xylopyranosyl-(1→4)-*α*-L-rhamnopyranosyl-(1→2)-*α*-L-arabinopyranoside], platycoside I [3-*O*-*β*-D-glucopyranosyl-(1→6)-*β*-D-glucopyranosyl-(1→6)-*β*-D-glucopyranosyl-2*β*,3*β*,16*α*,23-tetrahydroxyolean-12-en-28-oic acid 28-*O*-*β*-D-xylopyranosyl-(1→4)-*α*-L-rhamnopyranosyl-(1→2)-*α*-L-arabinopyranoside], platycoside J [3-*O*-*β*-D-glucopyranosyl-2*β*,3*β*,16*α*,23-tetrahydroxyolean-12-en-28-oic acid 28-*O*-*β*-D-xylopyranosyl-(1→4)-*α*-L-rhamnopyranosyl-(1→2)-*α*-L-arabinopyranoside], platycoside K [3-*O*-*β*-D-glucopyranosyl-(1→3)-*β*-D-glucopyranosyl-2*β*,3*β*,16*α*,23,24-pentahydroxyolean-12-en-28-oic acid], and platycoside L [3-*O*-*β*-D-glucopyranosyl-(1→6)-*β*-D-glucopyranosyl-2*β*,3*β*,16*α*,23,24-pentahydroxyolean-12-en-28 oic acid], and three known triterpenoid saponins, platycoside F, platycoside B, and platycoside C, were isolated from the roots of *Platycodon grandiflorum* A. DC. Their chemical structures were elucidated on the basis of their spectral data and chemical evidence.

Key words *Platycodon grandiflorum*; Campanulaceae; saponin; platycoside H; platycoside I; platycoside J

Platycodi Radix, the roots of *Platycodon grandiflorum* A. DC. (Campanulaceae), has been used in traditional Oriental medicine as an expectorant and antitussive to treat coughs, colds, upper respiratory tract infections, sore throats, tonsillitis, and chest congestion.[1,2] In northern China and Korea, P. radix is also used as a food. Chemical investigation of P. radix revealed that triterpenoid saponins[3—5] were the main chemical components. In a previous paper, we reported one new prosaponin, nine known saponin, and three known non-triterpenoidal compounds from the roots of *P. grandiflorum* A. DC.[6] Further investigation led to the isolation of five new triterpenoid saponins, platycosides H—L (**1**—**5**), from the roots of *P. grandiflorum*, together with three known triterpenoid saponins, platycoside F (**6**),[7] platycoside B (**7**),[4] and platycoside C (**8**).[4]

Results and Discussion

The 75% EtOH extract from the roots of *P. grandiflorum* were partitioned with aqueous EtOAc. The aqueous layer was separated by a macroreticular resin column to give the 60% EtOH eluates that upon drying afforded the total saponins. The total saponins were chromatographed on silica gel, a reversephase column, and finally on HPLC to afford compounds **1**—**8**.

Platycoside H (**1**) was a white amorphous powder, and its molecular formula was assigned to be $C_{58}H_{94}O_{28}$ based on the high-resolution (HR)-FAB-MS spectrum. The spectral features and physicochemical properties revealed **1** to be a triterpenoid saponin. The IR spectrum exhibited absorptions at 3420 cm^{-1} (OH), 1734 cm^{-1} (ester carbonyl), and 1651 cm^{-1} (double bond). The six tertiary methyl groups (δ 1.00, 1.16×2, 1.33, 1.56, 1.73 ppm) and one olefinic proton (δ 5.57, br s) were observed in the ^{1}H-NMR spectrum. The ^{13}C-NMR spectrum showed six sp^3 carbons at δ 15.3, 17.5, 17.6, 24.8, 27.2, and 33.3, two sp^2 olefinic carbons at δ 123.5 and 144.3, and four oxygenated methylene and methine carbons at δ 66.1, 69.7, 74.1, and 84.2 ppm (Table 1). The information on the ^{1}H-NMR spectrum coupled with the ^{13}C-NMR spectrum indicated that **1** has a 2*β*,3*β*,16*α*,23-tertahydroxyolean-12-en-28-oic acid (polygalacic acid) as an aglycon. The chemical shifts of C-3 (δ 84.2) and C-28 (δ 176.0) revealed that **1** was a bisdesmosidic glycoside. The ^{1}H- and ^{13}C-NMR spectra of **1** exhibited five sugar anomeric protons at δ 4.94 (d, J=8.0 Hz), 5.03 (d, J=8.0 Hz), 5.18 (d, J=7.0 Hz), 5.77 (br s), and 6.48 (d, J=2.5 Hz) and carbons at δ 105.0, 105.2, 106.9, 101.1, and 93.6 (Table 1). In the ^{1}H-NMR spectrum, one doublet methyl signal at δ 1.76 (J=5.5 Hz) belonging to rhamnose was observed. Acid hydrolysis of **1** gave arabinose, rhamnose, xylose, and glucose, which were analyzed by gas chromatography as their alditol acetates in a ratio of 1 : 1 : 1 : 2. The absolute configurations of sugars were shown to be L-arabinose, L-rhamnose, D-xylose, and D-glucose according to the method reported by Hara and coworkers.[8] All the monosaccharides of **1** were in pyranose forms, as determined by their ^{1}H- and ^{13}C-NMR spectral data as well as 2D NMR experiments. The *β*-anomeric configurations of the D-glucose and D-xylose units were determined by their $^3J_{H1,H2}$ coupling constants (7.0—8.0 Hz). The *α*-anomeric configurations of the L-arabinose was determined by its $^3J_{H1,H2}$ coupling constants (2.5 Hz) and $J_{C1,H1}$ coupling constant (170 Hz).[4,9] The L-rhamnose was determined to have the *α*-configuration based on the broad singlet of its anomeric proton.[4] The sequence of the glycan part connected to C-3 of the aglycon was deduced from the following HMBC correlations: H-1 (δ 4.94) of terminal glucose with C-6 (δ 70.0) of inner glucose, and H-1 (δ 5.03) of inner glucose with C-3 (δ 84.2) of sapogenin. The second bisdesmosidic part at C-28 was established based on HMBC correlations between H-1 (δ 5.18) of terminal xylose and C-4 (δ 83.6) of rhamnose, H-1 (δ 5.77) of rhamnose and C-2 (δ 75.5) of arabinose, and H-1 (δ 6.48) of arabinose and C-28 (δ 176.0) (Fig. 1). On the basis of the above evidence,

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Table 1. ^{13}C-NMR Data of Compounds **1**—**5** in Pyridine-d_5

Carbon	**1**[a]	**2**[b]	**3**[b]	**4**[b]	**5**[b]	Carbon	**1**[a]	**2**[b]	**3**[b]	**4**[b]	**5**[b]
1	44.1	44.2	44.3	45.0	45.2	Glc- (center)					
2	69.7	70.1	70.1	69.7	68.7	1′	105.0	105.1		105.7	105.0
3	84.2	88.8	83.6	85.3	87.6	2′	75.2	75.2		75.5	74.8
4	42.8	42.8	42.8	48.1	48.1	3′	78.6	78.5		78.7	78.6
5	47.6	47.7	47.9	47.2	47.3	4′	71.8	71.5		71.6	71.4
6	18.4	18.4	18.1	19.2	19.3	5′	78.3	77.0		78.3	77.9
7	33.3	33.3	33.4	33.7	33.6	6′	62.7	70.0		62.5	62.5
8	40.0	40.2	40.2	40.2	40.4	Glc- (terminal)					
9	47.6	47.6	47.7	47.2	49.0	1″		105.2			
10	37.0	37.0	37.0	37.4	38.0	2″		75.3			
11	24.0	24.0	24.1	24.2	24.0	3″		78.4			
12	123.5	123.5	123.0	122.6	122.8	4″		71.0			
13	144.3	144.3	144.4	145.1	145.0	5″		77.0			
14	42.3	42.3	42.3	42.3	42.5	6″		62.6			
15	36.0	36.0	36.0	36.1	36.0	Ara-					
16	74.1	74.1	74.1	74.0	74.7	1	93.6	93.6	93.6		
17	49.6	49.6	49.6	49.0	49.7	2	75.5	75.3	76.0		
18	41.3	41.3	41.3	41.6	41.7	3	70.2	71.6	70.6		
19	47.1	47.2	47.1	47.2	47.5	4	66.1	66.1	65.6		
20	30.9	30.9	30.9	31.1	31.1	5	63.1	63.1	63.1		
21	36.1	36.1	36.1	36.2	36.2	Rha-					
22	32.2	32.2	32.1	32.9	32.8	1	101.1	101.2	101.2		
23	66.1	66.1	66.2	63.5	63.0	2	71.6	71.4	71.6		
24	15.3	15.3	15.1	67.4	67.4	3	72.7	72.7	72.7		
25	17.6	17.6	17.6	18.0	19.0	4	83.6	83.7	83.1		
26	17.5	17.5	17.4	17.6	17.6	5	68.6	68.6	68.6		
27	27.2	27.2	27.2	27.2	27.1	6	18.4	18.4	18.4		
28	176.0	176.0	175.9	180.0	180.0	Xyl-					
29	33.3	33.3	33.3	33.3	33.3	1	106.9	106.9	106.8		
30	24.8	24.8	24.8	24.7	24.7	2	75.4	76.0	75.5		
Glc- (inner)						3	78.6	78.1	78.3		
1	105.2	105.5	105.7	105.7	106.1	4	71.0	69.6	71.0		
2	75.3	75.2	75.2	74.7	75.5	5	67.5	67.5	67.5		
3	78.5	78.6	78.6	88.6	78.6						
4	72.0	72.1	72.0	69.7	72.1						
5	76.7	76.7	78.2	78.2	76.5						
6	70.0	70.6	62.6	62.2	70.6						

a) 125 MHz; *b*) 150 MHz.

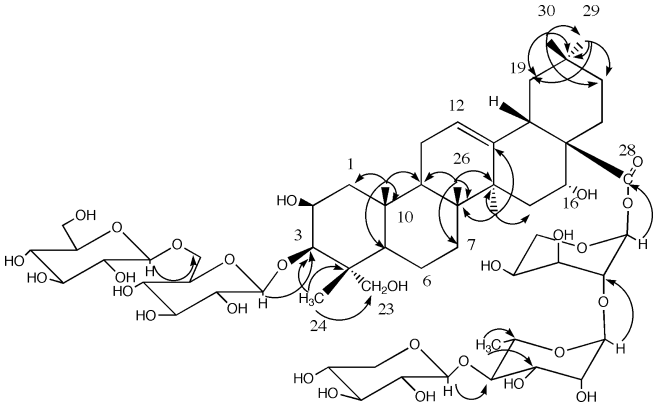
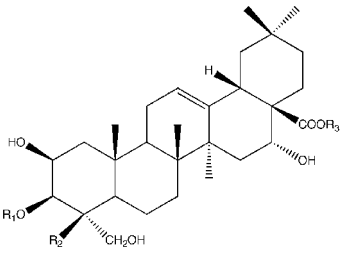


Fig. 1. The Structure and Selected HMBC Correlations of Platycoside H (**1**) (from H to C)

platycoside H (**1**) was identified to be 3-*O*-*β*-D-glucopyranosyl-(1→6)-*β*-D-glucopyranosyl-2*β*,3*β*,16*α*,23-tetrahydroxyolean-12-en-28-oic acid 28-*O*-*β*-D-xylopyranosyl-(1→4)-*α*-L-rhamnopyranosyl-(1→2)-*α*-L-arabinopyranoside.

Platycoside I (**2**) was shown to have the molecular formula $C_{64}H_{104}O_{33}$ based on its high-resolution (HR)-FAB-MS spectrum. The ^{1}H- and ^{13}C-NMR signals of **2** were assigned after DEPT, TOCSY, HMQC, and HMBC experiments. A comparison of the ^{1}H- and ^{13}C-NMR spectra of **2** with those **1** clearly revealed that the sapogenin of **2** was identical to that of **1**, and **2** was suggested to be a bisdesmosidic glycoside. The anomeric proton and carbon signals of one glucosyl group in the NMR spectra of **2** appeared, and the chemical shift of C-6 of the middle glucose in **2** was shifted downfield from δ 62.7 to 70.0. In comparison with **1**, the configurations of the monosaccharides in **2** were assigned for *β*-glucose, *α*-arabiose, *α*-rhamnose, and *β*-xylose, respectively. The spectral data showed that compound **2** is a glucosyl platycoside H. Acid hydrolysis of **2** gave arabinose, rhamnose, xylose, and glucose in a ratio of 1 : 1 : 1 : 3. On the basis of these results, platycoside I (**2**) was identified as 3-*O*-*β*-D-glucopyranosyl-(1→6)-*β*-D-glucopyranosyl-(1→6)-*β*-D-glucopyranosyl-2*β*,3*β*,16*α*,23-tetrahydroxyolean-12-en-28-oic acid 28-*O*-*β*-D-xylpyranosyl-(1→4)-*α*-L-rhamnopyranosyl-(1→2)-*α*-L-arabinopyranoside.

Platycoside J (**3**), an amorphous powder, has the molecular formula of $C_{52}H_{84}O_{23}$ based on its high-resolution FAB-MS spectrum. The ^{1}H- and ^{13}C-NMR signals of **3** were assigned after DEPT, TOCSY, HMQC, and HMBC experiments. A comparison of the ^{1}H- and ^{13}C-NMR spectra of **3** with those of **1** clearly revealed that the sapogenin of **3** was in identical



	R_1	R_2	R_3
1	Glc1-6Glc-	CH_3	-Ara2-1Rha4-1Xyl
2	Glc1-6Glc1-6Glc-	CH_3	-Ara2-1Rha4-1Xyl
3	Glc-	CH_3	-Ara2-1Rha4-1Xyl
4	Glc1-3Glc-	CH_2OH	H
5	Glc1-6Glc-	CH_2OH	H
6	Glc-	CH_2OH	-Ara2-1Rha4
7	Glc-	CH_2OH	-Ara2-1Rha(2-OAc)4-1Xyl
8	Glc-	CH_2OH	-Ara2-1Rha(3-OAc)4-1Xyl

Fig. 2. Structures of Compounds (**1**—**8**)

to that of **1**, and **3** was suggested to be a bisdesmosidic glycoside. The anomeric proton and carbon signals of one glucosyl group in the NMR spectra of **3** disappeared, and the chemical shift of C-6 of glucose in **3** was shifted upfield from δ 70.0 to 62.6. By comparison with **1**, the spectral data showed that compound **3** was a deglucosyl platycoside H. Acid hydrolysis of **3** gave arabinose, rhamnose, xylose, and glucose in a ratio of 1 : 1 : 1 : 1. On the basis of these results, platycoside J (**3**) was identified as 3-*O*-β-D-glucopyranosyl-2β,3β,16α,23-tetrahydroxyl-olean-12-en-28-oic acid 28-*O*-β-D-xylpyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranoside.

Platycoside K (**4**) was obtained as an amorphous powder, and its molecular formula was assigned to be $C_{42}H_{68}O_{17}$ based on the high-resolution-FAB-MS spectrum. The ^{1}H- and ^{13}C-NMR signals of **4** were assigned after DEPT, H–H COSY, HMQC, and HMBC experiments. A comparison of the ^{1}H- and ^{13}C-NMR signals of **4** with those of 3-*O*-β-laminaribiosyl platycodigenin methyl ester[10] clearly revealed that the aglycon of **4** was platycodigenin, and **4** had the same oligosaccharide moieties at C-3. Acid hydrolysis of **4** gave only glucose. Thus platycoside K (**4**) was identified to be 3-*O*-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-2β,3β,16α,23,24-pentahydroxyolean-12-en-28-oic acid.

Platycoside L (**5**) was obtained as an amorphous powder, and its molecular formula was assigned to be $C_{42}H_{68}O_{17}$ from the high-resolution-FAB-MS spectrum. The ^{1}H- and ^{13}C-NMR signals of **5** were assigned in DEPT, H–H COSY, HMQC, and HMBC experiments. A comparision of the ^{1}H- and ^{13}C-NMR signals of **5** with those of 3-*O*-β-gentiobiosyl platycodigenin methyl ester[10] clearly revealed that the aglycon of **5** was platycodigenin, and **5** had the same oligosaccharide moieties at C-3. Thus platycoside L (**5**) was identified as 3-*O*-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl-2β,3β,16α,23,24-pentahydroxy-olean-12-en-28-oic acid.

These two new monodesmosidic triterpenoid saponins (**4**, **5**) were reported to be the prosapogenin methyl esters.[10] Platycoside F (**6**),[7] platycoside B (**7**),[4] and platycoside C (**8**)[4] were identified by comparison of their spectra data with the data reported in the literature (IR, MS, ^{1}H-, ^{13}C-NMR).

Experimental

General Experimental Procedures Optical rotations were performed with a Perkin-Elmer 241MC polarimeter. FAB-MS and HR-FAB-MS spectral were recorded on a Jeol JMS-SX 102A mass spectrometer. IR spectra were measured with a Bruker IFS-55 infrared spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded with a Jeol a 500 NMR spectrometer. Chemical shifts were reported in parts per million on the d scale with TMS as an internal standard. Silica gel (Qingdao Haiyang Chemical Co., Ltd., 200—300 mesh) and Lichroprep RP-18 (Merck) were used for silical gel column chromatography and MPLC. Semipreparative HPLC was performed using an octadecyl silica (ODS) column (Pegasil ODS, Senshu Pak, 250 mm×10 mm i.d.) on a Hitachi liquid chromatography system with an RI detector. Gas-liquid chromatography was carried out on a Shimadzu GC-7A under the following conditions: column, 3% ECNSS-M (2 m×0.3 mm); column temperature, 190 °C; injection temperature, 210 °C; carrier gas, N_2; and flow rate, 25 ml/min. Spots were visualized by spraying with ethanol–10% H_2SO_4 and heating (110 °C, 5 min).

Plant Material The roots of *P. grandiflorum* were collected from Shenyang, Liaoning province, China, in 2003 and were taxonomically identified by Professor Sun Qishi of Shenyang Pharmaceutical University. A voucher specimen (no. 20030321) is deposited at the Shenyang Pharmaceutical University, School of Traditional Chinese Material Medica.

Extraction and Isolation The air-dried roots of *P. grandiflorum* (10 kg) were pulverized and extracted with ethanol (75%) three times under reflux. The combined extract was evaporated *in vacuo*, suspended in water, and then partitioned with EtOAc. The aqueous layer was chromatographed over a macroporous resin D101 column and eluted with H_2O, 60% EtOH, and 95% EtOH. The 60% EtOH elution was evaporated under a vacuum to obtain a residue (180 g). The residue (80 g) was chromatographed on silica gel (solvent, $CHCl_3$: MeOH = 50 : 1—1 : 1) to give six fractions (fr. A—F). Fraction B (27 g) was chromatographed on a silica gel column (solvent, $CHCl_3$: MeOH : H_2O = 30 : 10 : 1—6 : 4 : 1) to give a crude saponin subfraction. Further purification by MPLC [Lichroprep RP-18 (Merck), solvent, MeOH : H_2O = 1 : 1] and finally by semipreparative HPLC (MeOH : H_2O = 48 : 52) to give two new compounds **1** (9.5 mg) and **2** (5.2 mg). Fraction C (18 g) was chromatographed on a silica gel column (solvent, EtOAc : EtOH : H_2O = 9 : 1 : 0.5—85 : 15 : 7.5), followed by MPLC [Lichroprep RP-18 (Merck), solvent, MeOH : H_2O = 55 : 45] and finally by semipreparative HPLC (MeOH : H_2O = 52 : 48) to give three new compounds **3** (8.2 mg), **4** (5.5 mg), and **5** (5.6 mg) along with the three known compounds **6** (6.0 mg), **7** (8.1 mg), and **8** (6.6 mg).

Platycoside H (1) White amorphous powder; IR (KBr) cm^{-1}: 3420, 2927, 1734, 1651, 1042; FAB-MS *m/z*:1261.8 $[M+Na]^+$, 1277.8 $[M+K]^+$; HR-FAB-MS *m/z*: 1261.6479 $[M+Na]^+$ (Calcd for $C_{58}H_{94}O_{28}Na$, 1261.6307); ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 1.00, 1.16×2, 1.33, 1.56, 1.73 (each 3H, s, CH_3 of C-29, C-26, C-30, C-24, C-25, C-27), 1.76 (3H, d, J=5.5 Hz, CH_3 of Rha), 3.63, 4.43 (each 1H, d, J=11 Hz, H-23), 4.28 (1H, d, J=3.0 Hz, H-3), 4.83 (1H, m, H-2), 4.94 (1H, d, J=8.0 Hz, H-1′ of Glc), 5.03 (1H, d, J=8.0 Hz, H-1 of Glc), 5.18 (1H, d, J=7.0 Hz, H-1 of Xyl), 5.25 (1H, br s, H-16), 5.57 (1H, br s, H-12),5.77 (1H, br s, H-1 of Rha), 6.48 (1H, d, J= 2.5 Hz, H-1 of Ara). ^{13}C-NMR (125 MHz, pyridine-d_5) data: see Table 1.

Platycoside I (2) White amorphous powder; IR (KBr) cm^{-1}: 3410, 2929, 1737, 1637, 1039; FAB-MS *m/z*: 1439.8 $[M+K]^+$; HR-FAB-MS *m/z*: 1423.5749 $[M+Na]^+$ (Calcd for $C_{64}H_{104}O_{33}Na$, 1423.5361); ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 1.00, 1.15, 1.16, 1.34, 1.56, 1.72 (each 3H, s, CH_3 of C-29, C-30, C-26, C-24, C-25, C-27), 1.76 (3H, d, J=5.5 Hz, CH_3 of Rha), 3.63, 4.42 (each 1H, m, H-23), 4.27 (1H, m, H-3), 4.83 (1H, m, H-2), 4.78 (1H, d, J=7.5 Hz, H-1 of center Glc), 4.89 (1H, d, J=7.5 Hz, H-1 of inner Glc), 5.04 (1H, d, J=7.5 Hz, H-1 of terminal Glc), 5.19 (1H, d, J=7.5 Hz, H-1 of Xyl), 5.25 (1H, d, J=3.5 Hz, H-16), 5.56 (1H, br s, H-12), 5.77 (1H, br s, H-1 of Rha), 6.48 (1H, d, J=2.5 Hz, H-1 of Ara). ^{13}C-NMR (125 MHz, pyridine-d_5) data: see Table 1.

Platycoside J (3) White amorphous powder; IR (KBr) cm^{-1}: 3420, 2924, 1714, 1655, 1042; HR-FAB-MS *m/z*: 1099.5196 $[M+Na]^+$ (Calcd for $C_{52}H_{84}O_{23}Na$, 1099.5301); ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 1.00, 1.14, 1.17, 1.35, 1.59, 1.76 (each 3H, s, CH_3 of C-29, C-30, C-26, C-24, C-25, C-27), 1.76 (3H, d, J=6.0 Hz, CH_3 of Rha), 3.68, 4.42 (each 1H, m, H-23), 4.34 (1H, m, H-3), 4.83 (1H, m, H-2), 5.17 (1H, d, J=8.0 Hz, H-1 of Glc),

5.18 (1H, d, J=7.5 Hz, H-1 of Xyl), 5.26 (1H, br s, H-16), 5.64 (1H, br s, H-12), 5.78 (1H, br s, H-1 of Rha), 6.49 (1H, d, J=3.0 Hz, H-1 of Ara). ^{13}C-NMR (150 MHz, pyridine-d_5) data: see Table 1.

Platycoside K (4) White amorphous powder; IR (KBr) cm^{-1}: 3422, 2924, 1630, 1383, 1078; FAB-MS m/z: 867.4 $[M+Na]^+$, 845.8 $[M+H]^+$; HR-FAB-MS m/z: 867.44296 $[M+Na]^+$ (Calcd for $C_{42}H_{68}O_{17}Na$, 867.4353). ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 1.04, 1.08, 1.17, 1.52, 1.80 (each 3H, s, CH_3 of C-29, C-26, C-30, C-25, C-27), 4.02, 4.45 (each 1H, m, H-23), 4.26, 4.47 (each 1H, m, H-24), 4.54 (1H, m, H-3), 4.56 (1H, m, H-2), 4.90 (1H, d, J=8.0 Hz, H-1 of Glc), 5.22 (1H, d, J=8.0 Hz, H-1′ of Glc), 5.24 (1H, br s, H-16), 5.68 (1H, br s, H-12); ^{13}C-NMR (150 MHz, pyridine-d_5) data: see Table 1.

Platycoside L (5) White amorphous powder; IR (KBr) cm^{-1}: 3415, 2928, 1622, 1384, 1078; FAB-MS m/z: 867 $[M+Na]^+$, 845 $[M+H]^+$; HR-FAB-MS m/z: 867.42230 $[M+Na]^+$ (Calcd for $C_{42}H_{68}O_{17}Na$, 867.43537). ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 1.05, 1.07, 1.19, 1.43, 1.76 (each 3H, s, CH_3 of C-29, C-26, C-30, C-25, C-27), 3.93, 4.50 (each 1H, m, H-23), 4.28, 4.52 (each 1H, m, H-24), 4.55 (1H, m, H-3), 4.62 (1H, m, H-2), 4.86 (1H, d, J=7.0 Hz, H-1 of Glc), 4.89 (1H, d, J=8.0 Hz, H-1′ of Glc), 5.24 (1H, br s, H-16), 5.68 (1H, br s, H-12); ^{13}C-NMR (150 MHz, pyridine-d_5) data: see Table 1.

Acid Hydrolysis of 1—5 Compounds **1—5** (3 mg each) were heated in 1 ml of 1 M HCl (dioxane–H_2O, 1 : 1) at 90 °C for 3 h in a water bath. Dioxane was removed, the solution was extracted with EtOAc (1 ml×3), and the EtOAc was removed. The aglycons of **1**, **2**, and **3** were consistent with polygalacic acid by comparing with TLC (silica gel plate, $CHCl_3$: MeOH : H_2O : AcOH=7 : 3 : 1 : 1, visualization with ethanol–10%H_2SO_4 spraying, and then heating). The monosaccharide portions were analyzed using gas chromatography after conversion of the hydrolysates into the corresponding alditol acetates. The arabinitol, glucitol, rhamnitol, and xylitol acetates from compounds **1**, **2**, and **3** were detected in a ratio of 1 : 2 : 1 : 1, 1 : 3 : 1 : 1, and 1 : 1 : 1 : 1, respectively using gas chromatography analysis. The absolute configurations of the sugars were determined according to the method reported by Hara and coworkers[8] using gas chromatography with the following conditions: column, 3% ECNSS-M (2 m×0.3 mm); column tempetature, 190 °C; injection temperature, 210 °C; and retention times (min), D-xylose (11.1), L-arabinose (12.0), L-rhamnose (12.1), and D-glucose (17.9). Using the same method for compounds **4** and **5** (3 mg each), their aglycons were consisitent with those of platycodigenin by comparing the TLC results. The only monosaccharide identified was glucitol acetate.

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