Chemical Constituents of the Aerial Parts of *Schnabelia tetradonta*

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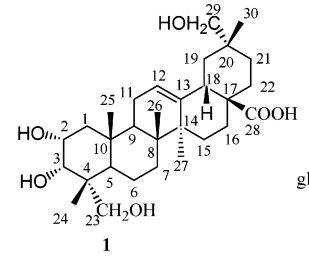
A phytochemical study on the ethanol extract of the aerial parts of *Schnabelia tetradonta* led to the isolation of five new compounds, **1**−**5**, together with seven known compounds. The structures of the new compounds were elucidated on the basis of spectral data interpretation as 2α,3α,23,29-tetrahydroxyolean-12-en-28-oic acid (**1**), 3-*O*-*β*-D-glucuronopyranosyl-2*β*,3*β*,16*β*-trihydroxy-28-norolean-12-en-15-on-23-oic acid (**2**), 21-*O*-*β*-D-glucopyranosyl-3*β*,21α,30-trihydroxyolean-13(18)-en-24-oic acid (**3**), 6-*C*-*β*-L-arabinopyranosyl-8-*C*-α-L-arabinopyranosylapigenin (**4**), and 4-acetylaminoethylphenyl 1-*O*-[6-*O*-(*Z*)-*p*-methoxycinnamoyl-*β*-D-glucopyranosyl(1→2)]-[*β*-D-glucopyranosyl(1→3)]-α-L-rhamnopyranoside (**5**), respectively.

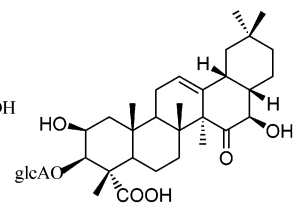
Schnabelia tetradonta (Sun) C. Y. Wu et C. Chen (Lamiaceae), commonly called "Jin Gu Cao", is an endemic herbaceous plant distributed in the southwest region of the People's Republic of China. It is used as a febrifuge to relieve internal fevers and as a remedy for rheumatism treatment in traditional Chinese medicine.[1] No previous phytochemical investigation on this species has been conducted. The medicinal uses of *S. tetradonta* prompted us to investigate its polar components in the ethanol extract of the aerial parts, resulting in the isolation of three new oleanane triterpenoids, **1**−**3**, a new apigenin di-*C*-glycoside, **4**, and a new aminoethylphenyl oligoglycoside, **5**, together with seven known compounds, anchoic acid,[2] apigenin,[3] sitosterol,[4] daucosterol,[4] mussaenoside,[5] martynoside,[6] and apigenin 6,8-di-*C*-α-L-arabinopyranoside.[7] This paper deals with the isolation and structural elucidation of the five new compounds.

Results and Discussion

The molecular formula ($C_{30}H_{48}O_6$) of compound **1** was obtained from the HRESIMS at *m*/*z* 527.3356 $[M + Na]^+$. Its ^1H NMR spectrum showed the presence of five singlet methyl signals (*δ* 0.77, 0.82, 0.92, 1.01, 1.18), a double doublet (*δ* 2.88, *J* = 4.2, 14.0 Hz), and a broad singlet (*δ* 5.26) due to H-18 and H-12, suggesting the presence of an olean-12-ene skeleton.[8] The ^{13}C NMR data for **1** revealed the presence of two secondary carbinol carbons (*δ* 67.2, 78.7) and two primary carbinol carbons (*δ* 71.3, 74.4). By comparison of the ^{13}C NMR data for **1** with those for esclentic acid[9] and mesembryanthemoidigenic acid,[8] **1** could be assigned with the same A ring moiety as the former and the same E ring moiety as the latter. Therefore, the hydroxyl groups were located at C-2α, C-3α, C-23, and C-29. The correlations observed in the HMBC spectrum of H-3 (*δ* 3.60) with C-2 (*δ* 67.2), H-23 (*δ* 3.52, 3.38) with C-3 (*δ* 78.7) and C-24 (*δ* 17.8), and H-30 (*δ* 0.92) with C-29 (*δ* 74.4) confirmed the location of the hydroxyl groups (Figure 1). The relatively large *trans*-diaxial coupling constant for H-2 (*J* = 11.0 Hz) and the small coupling constant for H-3 (*J* = 3.0 Hz) indicated that the OH-2 and OH-3 are α-equatorial and α-axial, respectively. Therefore, the structure of **1** was elucidated as 2α,3α,23,29-tetrahydroxyolean-12-en-28-oic acid.



1



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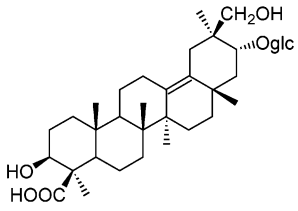

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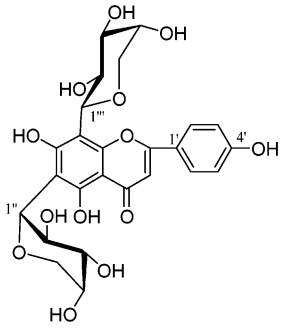

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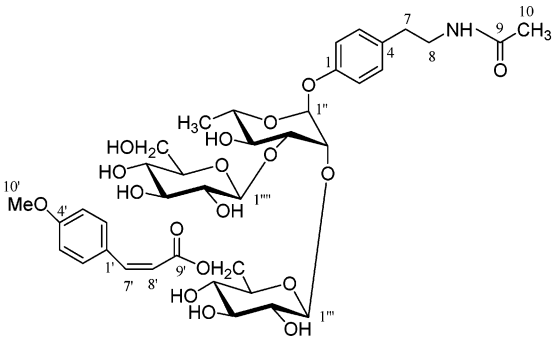

5

The molecular formula ($C_{35}H_{52}O_{12}$) of compound **2** was obtained from the HRESIMS at *m*/*z* 665.3560 $[M + H]^+$. The ESIMS-MS fragment ion at *m*/*z* 487 obtained from the quasimolecular ion at *m*/*z* 663 $[M - H]^-$ indicated the loss of a hexuronic acid unit, which was identified as glucuronic acid by TLC upon acid hydrolysis. Its *β*-anomeric configuration was assigned from the large $^3J_{1',2'}$ coupling constant (*J* = 7.6 Hz), and the configuration of the sugar was chosen consistent with that most commonly encountered among

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Table 1. ^{1}H and ^{13}C NMR Data and HMBC Correlations for Compounds **2** and **3** (in C_5D_5N)

	2			**3**		
position	δ_C	δ_H (J_{HH} in Hz)	HMBC	δ_C	δ_H (J_{HH} in Hz)	HMBC
1	44.4 t	1.29 m, 2.32 d (13.5)	H-25	39.8 t	1.01 m, 1.78 m	H-25
2	70.5 d	4.88 m	H-1	29.2 t	1.96 m, 2.47 m	H-3
3	86.1 d	4.75 d (3.6)	H-1, 2, 24, 1′	78.0[a] d	3.37 dd (4.5, 11.9)	H-23
4	52.8 s		H-2, 3, 24	49.2 s		H-3, 5, 23
5	52.3 d	2.12 m	H-7, 25	56.6 d	1.01 m	H-23, 25
6	21.2 t	1.98 m	H-7	20.8 t	2.05 m, 2.13 m	H-7
7	36.1 t	2.09 m	H-5, 26	35.2 t	1.39 m, 1.45 m	H-26
8	41.6 s		H-6, 26, 27	44.7 s		H-26, 27
9	47.8 d	1.62 m	H-12, 25, 26	50.4 d	1.46 m	H-25, 26
10	36.9 s		H-25	38.0 s		H-9, 25
11	23.9 t	1.98 m, 2.10 m	H-9, 12	22.4 t	1.14 m, 1.87 m	H-9
12	125.1 d	5.43 brs	H-11	25.6 t	2.69 brd (12.7)	
13	142.2 s		H-11, 18, 27	135.5 s		H-19, 27
14	54.6 s		H-12, 16, 26, 27	41.1 s		H-9, 27
15	214.7 s		H-16, 17, 27	26.6 t	1.01 m, 1.63 m	H-27
16	76.0 d	4.48 brs		36.7 t	1.28 m, 1.39 m	H-28
17	44.1 d	2.64 m	H-19	36.2 s		H-19, 22, 28
18	45.8 d	2.84 m	H-12, 17, 19	131.8 s		H-19, 22, 28
19	46.8 t	1.34 m, 1.12 m	H-18, 29, 30	33.6 t	2.42 brd (14.4) 2.58 brd (14.4)	H-29, 30
20	30.9 s		H-19, 21, 29, 30	43.1 s		H-19, 21, 22, 29, 30
21	34.5 t	1.13 m, 1.72 m	H-17, 22, 29, 30	76.2 d	4.54 dd (4.8, 12.5)	H-1′, 19, 22, 29, 30
22	21.2 t	1.94 m		44.9 t	1.54 t (12.5), 1.96 m	H-28
23	180.4 s		H-3, 24	24.7[b] q	1.70 s	H-3
24	14.2 q	2.05 s	H-3, 5	180.6 s		H-3, 23
25	17.0 q	1.64 s	H-5	14.8[c] q	1.07 s	H-9
26	18.1 q	1.19 s	H-9	18.0 q	0.84 s	H-9
27	20.6 q	1.24 s	H-7	21.4 q	1.17 s	
28				24.6[b] q	1.03 s	H-22
29	33.3 q	0.78 s	H-19, 30	14.7[c] q	0.83 s	H-19, 21, 30
30	23.2 q	0.83 s	H-19, 21	68.4 t	3.46 d (11.0) 4.40 d (11.0)	H-21, 29
	β-GlcA			*β*-Glc		
1′	105.9 d	5.24 d (7.6)	H-2′, 3′, 5′	104.4 d	4.97 d (7.8)	H-5′, 21
2′	74.9 d	3.99 m	H-3′	75.0 d	4.06 m	H-3′
3′	77.7 d	4.21 t (8.8)	H-2′	78.7 d	4.30 t (8.7)	H-2′
4′	73.2 d	4.50 m	H-5′, 3′	72.7 d	4.04 m	H-3′, 5′
5′	77.4 d	4.61 d (9.7)	H-4′	78.2[a] d	4.11 m	H-1′, 6′
6′	172.8 s		H-4′, 5′	63.6 t	4.19 d (11.0), 4.70 dd (1.9, 11.0)	H-4′

[a,b] Values bearing the same superscript may be interchanged.

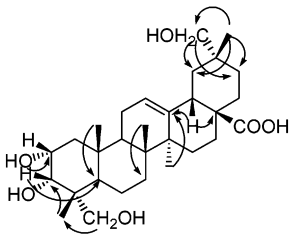

Figure 1. Key HMBC correlations for **1**.

plant glycosides. The ^{1}H and ^{13}C NMR spectra of **2** indicated the presence of a norolean-12-ene type aglycon,[10] containing six tertiary methyls (*δ* 2.05, 1.64, 1.19, 1.24, 0.78, 0.83), a carboxyl group (*δ* 180.4), a keto function (*δ* 214.7), and three secondary carbinol carbons (*δ* 70.5, 86.1, 76.0). A comparison of the ^{13}C NMR data for **2** with those for zanhic acid 3-glucuronide suggested that they have the same A ring moiety,[11] which was supported by 2D NMR experiments (^{1}H−^{1}H COSY, HMQC, HMBC, and NOESY). The carbonyl group was located at C-15 due to the correlations of H-27 (*δ* 1.24) and H-17 (*δ* 2.64) with C-15 (*δ* 214.7) in the HMBC spectrum (Table 1). The presence of a OH-16*β* was confirmed by the correlations of H-16 (*δ* 4.48) with C-14 (*δ* 54.6) and C-15 (*δ* 214.7) in the HMBC spectrum and the correlation of H-16 (*δ* 4.48) with H-27 (*δ* 1.24) in the NOESY spectrum (Figure 2). Both H-17 and H-18 were assigned with a *β*-configuration due to the correlations of H-18 (*δ* 2.84) with H-12 (*δ* 5.43) and H-17 (*δ* 2.64) in the

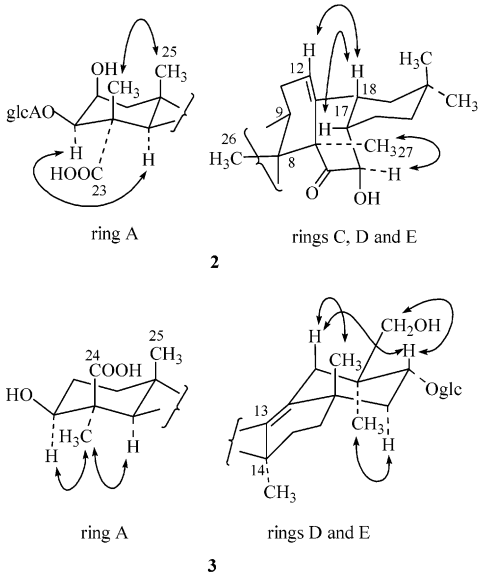

Figure 2. Key NOESY correlations for **2** and **3**.

NOESY spectrum. Therefore, **2** was elucidated as 3-*O*-*β*-D-glucuronopyranosyl-2*β*,3*β*,16*β*-trihydroxy-28-norolean-12-en-15-on-23-oic acid.

The molecular formula ($C_{36}H_{58}O_{10}$) of compound **3** was obtained from the HRESIMS at *m*/*z* 673.3937 $[M + Na]^+$. The ^{1}H and ^{13}C NMR spectra of **3** showed the presence of

a glucose unit (δ_H 4.97, J = 7.8 Hz; δ_C 104.4). In addition, its ^{1}H and ^{13}C NMR spectra indicated the presence of six tertiary methyls (δ 1.70, 1.07, 0.84, 1.17, 1.03, 0.83), a carboxyl group (δ 180.6), a primary carbinol carbon (δ 68.4), two secondary carbinol carbons (δ 78.0, 76.2), and two quaternary olefinic carbons (δ 135.5, 131.8) in the aglycon, suggesting that the aglycon possessed an olean-13(18)-ene skeleton.[12] The position of the double bond was confirmed by the correlations between H-27 (δ 1.17) and C-13 (δ 135.5) and between H-28 (δ 1.03) and C-18 (δ 131.8) in the HMBC spectrum (Table 1). The presence of OH-3 and COOH-24 was deduced from the relatively downfield signal of C-4 (δ 49.2) as well as the correlations of H-3 (δ 3.37) and H-23 (δ 1.70) with the carbonyl carbon (δ 180.6) in the HMBC spectrum. The hydroxyl group at C-3 was assigned as β-equatorial due to the large *trans*-diaxial coupling constant of H-3 (J = 11.9 Hz), and the carboxyl group at C-24 was confirmed by the correlations of H-23 (δ 1.70) with H-3 (δ 3.37) and H-5 (δ 1.01) in the NOESY spectrum. Correlations in the HMBC spectrum of H-30 (δ 3.46, 4.40) with C-29 (δ 14.7) and C-21 (δ 76.2) together with the observation of the NOESY correlation of H-22α (δ 1.54) with H-29 (δ 0.83) revealed the presence of a hydroxyl group at C-30. The sugar moiety was shown to be attached α-equatorially to the C-21 hydroxyl group from the correlation of C-21 with H-1′ (δ 4.97) of the glucose unit in the HMBC spectrum and the correlations observed in the NOESY spectrum of H-19β (δ 2.58) with H-21 (δ 4.54) and H-28 (δ 1.03) (Figure 2). Thus, the structure of **3** was elucidated as 21-*O*-β-D-glucopyranosyl-3β,21α,30-trihydroxyolean-13(18)-en-24-oic acid.

The molecular formula ($C_{25}H_{26}O_{13}$) of compound **4** was obtained from the HRESIMS at *m/z* 535.1442 $[M + H]^+$. An ESIMS-MS experiment of the quasimolecular ion at *m/z* 533 $[M - H]^-$ gave three daughter ions at *m/z* 515 $[M - H - 18]^-$, 473 $[M - H - 60]^-$, and 443 $[M - H - 90]^-$, corresponding to the typical fragmentation of a *C*-glycoside.[13] A 6,8-di-*C*-substituted apigenin skeleton of **4** was suggested by the appearance in the ^{1}H NMR spectrum of a singlet (δ 6.84, 1H), typical of H-3 of a flavone, two doublets (δ 6.88, 8.30, each 2H, J = 8.0 Hz), indicating a 4′-substituted phenyl ring, and an anomeric doublet (δ 4.58) and an anomeric broad singlet (δ 5.28), corresponding to two sugar residues.[7] Apart from 15 aromatic carbon signals for the apigenin skeleton in the ^{13}C NMR spectrum of **4**, the remaining 10 signals were ascribable to one β-L-arabinopyranosyl unit and one α-L-arabinopyranosyl unit.[14] The glycosidation sites for the β-L-arabinose at C-6 and the α-L-arabinose at C-8 of the aglycon were confirmed by the correlations between H-1″ (δ 5.28, brs) of the β-L-arabinose unit and C-5 (δ 157.4), C-6 (δ 106.9) and C-7 (δ 162.3), H-1‴ (δ 4.58, d, J = 9.8 Hz) of the α-L-arabinose unit and C-7 (δ 162.3), C-8 (δ 104.9), and C-9 (δ 155.2) in the HMBC spectrum (Figure 3). Therefore, the structure of **4** was determined as 6-*C*-β-L-arabinopyranosyl-8-*C*-α-L-arabinopyranosylapigenin.

The molecular formula ($C_{38}H_{51}NO_{18}$) of compound **5** was obtained from the HRESIMS at *m/z* 810.3172 $[M + H]^+$. Three anomeric proton signals in the ^{1}H NMR spectrum at δ 6.27 (brs), 5.44 (d, J = 8.0 Hz), and 5.49 (d, J = 7.7 Hz) suggested the occurrence of three sugar residues, which were identified by TLC upon acid analysis as L-rhamnose and D-glucose. The ^{1}H NMR spectrum (Table 2) showed the signals for a *cis*-coumaroyl moiety, an AA′XX′ system for H-3′, 5′ and H-2′, 6′ (δ 6.94, 7.92, J = 8.8 Hz), and an AX system for H-7′ and H-8′ (δ 6.76, 5.77, J = 12.9 Hz). In addition, the ^{1}H NMR spectrum indicated the presence of another aromatic ring moiety (δ 7.14), two coupled methylene moieties (δ 2.83, 3.60), an acylamino group (δ 8.50), an acetyl (δ 2.01), and a methoxy group (δ 3.62). The ^{13}C NMR spectrum was in accordance with those deductions, from which 11 corresponding carbons were observed. The four protons at δ 7.14 were assigned at C-2, 6 (δ 117.1) and C-3, 5 (δ 130.2), respectively, due to the cross-peaks observed in the HMQC and HMBC spectra (Table 2). The correlations in the HMBC spectrum between the carbonyl C-9 (δ 170.0) and NH (δ 8.50) and H-8 (δ 3.60), together with the observation of the ^{1}H−^{1}H COSY correlation of NH with H-8, which in turn was correlated to H-7 (δ 2.83), provided key evidence for the establishment of the structure of the aglycon of **5**. Furthermore, correlations observed in the HMBC spectrum between H-1″ (δ 6.27) of the

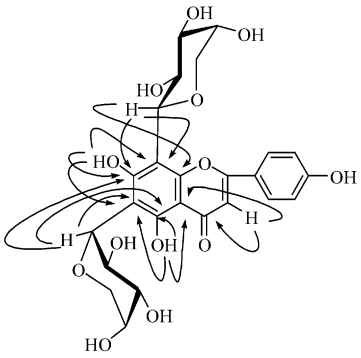

Figure 3. Key HMBC correlations for **4**.

Table 2. ^{1}H and ^{13}C NMR Data and HMBC Correlations for Compound **5** (C_5D_5N)

position	δ_C	δ_H (J_{HH} in Hz)	HMBC
1	155.5 s		H-3, 5, 1″
2, 6	117.1 d	7.14 s	H-3, 5
3, 5	130.2 d	7.14 s	H-2, 6, 7
4	133.7 s		H-2, 6, 7, 8
7	35.4 t	2.83 t (7.0)	H-3, 5, 8
8	41.4 t	3.60 t (7.0)	H-7, NH
NH		8.50 t (5.7)	
9	170.0 s		H-8, 10, NH
10	23.0 q	2.01 s	
1′	127.8 s		H-3′, 5′, 8′
2′, 6′	133.1 d	7.92 d (8.8)	H-7′
3′, 5′	114.0 d	6.94 d (8.8)	H-2′, 6′
4′	161.0 s		H-10′
7′	143.7 d	6.76 d (12.9)	H-2′, 6′
8′	116.9 d	5.77 d (12.9)	H-7′
9′	166.5 s		H-7′, 8′, 6‴
10′	55.2 q	3.62 s	
α-Rha			
1″	98.9 d	6.27 brs	
2″	79.7 d	4.94 m	H-1‴
3″	81.1 d	4.82 dd (3.3, 9.5)	H-1″, 2″, 4″, 1⁗
4″	72.3 d	4.36 m	H-2″, 3″
5″	70.2 d	4.19 m	H-1″, 6″
6″	18.2 q	1.35 d (6.0)	H-4″
β-Glc			
1‴	106.2 d	5.44 d (8.0)	H-2″, 2‴
2‴	75.8 d	4.07 m	H-3‴
3‴	78.0[a] d	4.24 m	H-1‴, 5‴
4‴	71.3[b] d	4.07 m	H-5‴, 6‴
5‴	75.2 d	4.07 m	H-4‴, 6‴
6‴	64.4 t	4.72 dd (5.2, 11.7), 5.06 m	
β-Glc			
1⁗	105.6 d	5.49 d (7.7)	H-2⁗, 3″
2⁗	75.5 d	4.13 m	H-3⁗
3⁗	78.2[a] d	4.24 m	H-4⁗
4⁗	71.4[b] d	4.23 m	H-3⁗
5⁗	78.4 d	3.89 m	H-1⁗, 4⁗, 6⁗
6⁗	62.4 t	4.42 m, 4.34 m	H-4⁗

[a,b] Values bearing the same superscript may be interchanged.

rhamnose and C-1 (δ 155.5) of the aglycon, H-1‴ (δ 5.44) of the glucose unit and C-2″ (δ 79.7) of the rhamnose, and H-1⁗ (δ 5.49) of another glucose unit and C-3″ (δ 81.1) of the rhamnose allowed the determination of the sequence of the trisaccharide chain at C-1 as β-D-glucopyranosyl-(1→2)-[β-D-glucopyranosyl(1→3)]-α-L-rhamnopyranose. Finally, a HMBC correlation of H-6‴ (δ 4.72, 5.06) with the carbonyl C-9′ (δ 166.5) confirmed that the methoxycinnamoyl unit was attached to C-6‴ (δ 64.4) of the glucose unit. Therefore, **5** was established as 4-acetylaminoethylphenyl 1-*O*-[6-*O*-(*Z*)-*p*-methoxycinnamoyl-β-D-glucopyranosyl(1→2)]-[β-D-glucopyranosyl(1→3)]-α-L-rhamnopyranoside. This structure was supported by the ESIMS-MS analysis of the deacylated product after basic hydrolysis. Consecutive multistage collisionally activated decomposition MS experiments of the quasimolecular ion at *m/z* 650 $[M + H]^+$ gave the fragment ions at *m/z* 488, 326, 180, and 138, corresponding to the sequential loss of two glucose and one rhamnose unit and an acetyl group.

Experimental Section

General Experimental Procedures. Melting points were determined on a XRC-1 apparatus and are uncorrected. Optical rotations were measured with a PE-241 polarimeter. IR spectra were recorded as KBr pellets on a Nicolet MX-1 spectrometer. The NMR spectra were run on a Bruker AM-400 instrument with TMS as the internal standard. MS were performed on Bruker Dalonics Apex II (HRESIMS) and Finnigen LCQ^{DECA} (ESIMS and MS−MS) mass spectrometers, respectively. Column chromatography was carried out on silica gel (200−300 mesh, Qingdao Marine Chemical Co., Qingdao, People's Republic of China), MCI CHP-20 gel, and ODS (Merck). TLC was performed on precoated plates (GF254 Qingdao Marine Chemical Co.) and RP-18 254 (Merck) with the following solvent systems: A, $CHCl_3$−MeOH (10:1, 5:1, 3:1, and 2:1); B, petroleum ether−Me_2CO (3:2); and C, MeOH−H_2O (8:2, 7:3, and 5:5).

Plant Material. The plant was collected from Yibin, Sichuan, People's Republic of China, in August 2000, and identified as *Schnabelia tetradonta* (Sun) C. Y. Wu et C. Chen by Prof. Z. Y. Liu and Prof. Z. C. Zhao. A voucher specimen (No. 20000825) was deposited in the herbarium of Chengdu Institute of Biology, Chinese Academy of Science.

Extraction and Isolation. Dried and powdered aerial parts of *S. tetradonta* (10 kg) were extracted with 95% EtOH at room temperature to give an extract (700 g), which was suspended in H_2O and extracted with petroleum ether, EtOAc, and *n*-BuOH successively. The EtOAc extract (15 g) was separated by column chromatography on MCI CHP-20 with a gradient system of MeOH−H_2O (6:4, 7:3, 8:2, 9:1, and 10:0) to yield four fractions. Fraction 1 was subjected to silica gel chromatography with petroleum ether−EtOAc mixtures of increasing polarity (7:1 to 1:1) to yield anchoic acid[2] (31 mg). Compound **1** (7 mg) was obtained from fraction 2 by further chromatography on silica gel eluted with petroleum ether−Me_2CO (1:1). Apigenin[3] (2 mg) and sitosterol[4] (120 mg) were isolated from fraction 3 by chromatography on silica gel eluted with petroleum ether−EtOAc (1:1). The *n*-BuOH extract (68 g) was separated by chromatography on silica gel with $CHCl_3$−MeOH mixtures of increasing polarity (10:1 to 1:1) to yield eight fractions. Daucosterol[4] (58 mg) was afforded from fraction 2 after purification on a silica gel column with $CHCl_3$−MeOH (8:1). Fraction 3 was further separated by chromatography on silica gel with $CHCl_3$−MeOH (8:1) to yield three fractions, of which fraction 2 afforded **2** (26 mg) and mussaenoside[5] (210 mg) after purification on a silica gel column with $CHCl_3$−MeOH (8:1). Fraction 4 was separated on an ODS column with a MeOH−H_2O gradient system (3:7 to 8:2) to yield seven fractions, of which fraction 4 afforded martynoside[6] (160 mg) after further chromatography on silica gel with EtOAc−2-propanol (12:1), and fraction 5 yielded **5** (62 mg) by crystallization. Fraction 5 was separated on silica gel column with $CHCl_3$−MeOH (4:1) to yield 10 fractions, of which fraction 2 yielded **3** (10 mg), and fraction 7 was chromatographed on a silica gel column with $CHCl_3$−MeOH (4:1) to yield **4** (15 mg) and apigenin 6,8-di-*C*-α-L-arabinopyranoside[7] (240 mg).

2α,3α,23,29-Tetrahydroxyolean-12-en-28-oic acid (1): white needles (MeOH); mp 271−273 °C; $[\alpha]^{20}_D$ +22.4° (*c* 0.20, MeOH); IR (KBr) ν_{max} 3432, 2935, 1698, 1634, 1388 cm^{-1}; ^1H NMR (CD_3OD) δ 5.26 (1H, brs, H-12), 3.87 (1H, dt, *J* = 3.0, 11.0 Hz, H-2), 3.60 (1H, d, *J* = 3.0 Hz, H-3), 3.52 (1H, d, *J* = 11.0 Hz, H-23), 3.38 (1H, d, *J* = 11.0 Hz, H-23), 3.18 (2H, s, H-29), 2.88 (1H, dd, *J* = 4.2, 14.0 Hz, H-18), 1.93 (2H, m, H-11), 1.56 (1H, m, H-1), 1.26 (1H, m, H-1), 1.18 (3H, s, H-27), 1.01 (3H, s, H-25), 0.92 (3H, s, H-30), 0.82 (3H, s, H-26), 0.77 (3H, s, H-24); ^{13}C NMR (CD_3OD) δ 181.8 (s, C-28), 145.3 (s, C-13), 123.6 (d, C-12), 78.7 (d, C-3), 74.4 (t, C-29), 71.3 (t, C-23), 67.2 (d, C-2), 49.3 (d, C-9), 47.9 (s, C-17), 44.2 (d, C-5), 43.0 (s, C-14), 42.5 (s, C-4), 42.2 (t, C-1), 42.0 (d, C-18), 41.4 (t, C-19), 40.6 (s, C-8), 39.2 (s, C-10), 36.8 (s, C-20), 33.5 (t, C-7), 33.1 (t, C-22), 29.3 (t, C-21), 28.8 (t, C-15), 26.5 (q, C-27), 24.6 (t, C-16), 24.1 (t, C-11), 19.5 (q, C-30), 19.0 (t, C-6), 17.8 (q, C-24), 17.6 (q, C-26), 17.2 (q, C-25); HRESIMS *m/z* 527.3356 $[M + Na]^+$ (calcd for $C_{30}H_{48}O_6Na$, 527.3349); R_f 0.45 [$CHCl_3$−MeOH (5:1)].

3-*O*-β-D-Glucuronopyranosyl-2β,3β,16β-trihydroxy-28-norolean-12-en-15-on-23-oic acid (2): white needles (MeOH); mp >350 °C; $[\alpha]^{25}_D$ +54.5° (*c* 0.44, MeOH); IR (KBr) ν_{max} 3447, 2924, 1708, 1634, 1384 cm^{-1}; ^1H NMR and ^{13}C NMR data, see Table 1; HRESIMS *m/z* 665.3560 $[M + H]^+$ (calcd for $C_{35}H_{53}O_{12}$, 665.3537); ESIMS-MS *m/z* 663 $[M - H]^-$, 487 $[M - H - 176]^-$; R_f 0.42 [$CHCl_3$−MeOH (4:1)].

21-*O*-β-D-Glucopyranosyl-3β,21α,30-trihydroxyolean-13(18)-en-24-oic acid (3): amorphous white powder (MeOH); mp 270−272 °C; $[\alpha]^{25}_D$ −11.7° (*c* 0.41, MeOH); IR (KBr) ν_{max} 3426, 2935, 1697, 1638, 1381 cm^{-1}; ^1H NMR and ^{13}C NMR data, see Table 1; HRESIMS *m/z* 673.3937 $[M + Na]^+$ (calcd for $C_{36}H_{58}O_{10}Na$, 673.3922); R_f 0.44 [$CHCl_3$−MeOH (4:1)].

6-*C*-β-L-Arabinopyranosyl-8-*C*-α-L-arabinopyranosyl-apigenin (4): amorphous yellow powder (MeOH); mp 206−208 °C; $[\alpha]^{25}_D$ −42.0° (*c* 0.55, DMSO); IR (KBr) ν_{max} 3421, 2923, 1649, 1576, 1511, 1290 cm^{-1}; ^1H NMR (DMSO-d_6) δ 14.00 (1H, s, OH-5), 10.30 (1H, s, OH-4′), 10.14 (1H, s, OH-7), 8.30 (2H, d, *J* = 8.0 Hz, H-2′, -6′), 6.88 (2H, d, *J* = 8.0 Hz, H-3′, -5′), 6.84 (1H, s, H-3), 5.28 (1H, brs, H-1″), 4.58 (1H, d, *J* = 9.8 Hz, H-1‴); ^{13}C NMR (DMSO-d_6) δ 182.3 (s, C-4), 164.3 (s, C-2), 162.3 (s, C-7), 161.2 (s, C-4′), 157.4 (s, C-5), 155.2 (s, C-9), 129.7 (d, C-2′, 6′), 121.0 (s, C-1′), 116.0 (d, C-3′, 5′), 106.9 (s, C-6), 104.9 (s, C-8), 103.3 (s, C-10), 101.9 (d, C-3), 75.1 (d, C-3‴), 74.6 (d, C-1‴), 71.9 (d, C-3″), 71.3 (t, C-5‴), 70.8 (d, C-1″), 69.2 (d, C-4″), 69.9 (d, C-4‴), 68.1 (d, C-2‴), 66.6 (t, C-5″), 63.2 (d, C-2″); HRESIMS *m/z* 535.1442 $[M + H]^+$ (calcd for $C_{25}H_{27}O_{13}$, 535.1446); ESIMS-MS *m/z* 533 $[M - H]^-$, 515 $[M - H - 18]^-$, 473 $[M - H - 60]^-$, 443 $[M - H - 90]^-$, 383 $[M - H - 90-60]^-$, 353 $[M - H - 90-90]^-$; R_f 0.31 [$CHCl_3$−MeOH (2:1)].

4-Acetylaminoethylphenyl 1-*O*-[6-*O*-(*Z*)-*p*-methoxycinnamoyl-β-D-glucopyranosyl(1→2)]-[β-D-glucopyranosyl-(1→3)]-α-L-rhamnopyranoside (5): white needles (MeOH); mp 198−199 °C; $[\alpha]^{25}_D$ −14.1° (*c* 0.75, MeOH); IR (KBr) ν_{max} 3497, 3362, 2927, 1716, 1655, 1604, 1511 cm^{-1}; ^1H NMR and ^{13}C NMR data, see Table 2; HRESIMS *m/z* 810.3172 $[M + H]^+$ (calcd for $C_{38}H_{52}NO_{18}$, 810.3179); R_f 0.50 [$CHCl_3$−MeOH (4:1)].

TLC Analysis of Sugars of Compounds 2, 3, and 5. Compounds **2**, **3**, and **5** were each applied to a TLC plate and then hydrolyzed under HCl vapor at 60 °C for 40 min. After the excess HCl was removed, the authentic sugars were applied to the same plate. TLC plates were developed by $CHCl_3$−MeOH−H_2O−CH_3COOH (16:9:2:2), sprayed with aniline−phthalic acid, and heated. Hexoses and hexuronic acids gave purple spots. The R_f values of each sugar were as follows: glucuronic acid, 0.18; glucose, 0.42; rhamnose, 0.57.

Basic Hydrolysis of Compound 5. Compound **5** (3 mg) was heated in 5 M $NH_3 \cdot H_2O$ for 4 h at 110 °C in a sealed tube. The mixture was adjusted to pH 6 with 1 M aqueous HCl and then extracted with *n*-BuOH (10 mL × 2). The water phase

was concentrated, and the residue was subjected to MS−MS analysis: ESIMS-MS *m/z* 650 $[M + H]^+$, 488 $[M + H - 162]^+$, 326 $[M + H - 162 - 162]^+$, 180 $[M + H - 162 - 162 - 146]^+$, 138 $[M + H - 162 - 162 - 146 - 42]^+$.

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