Chemical Constituents from the Roots of *Schnabelia tetradonta*

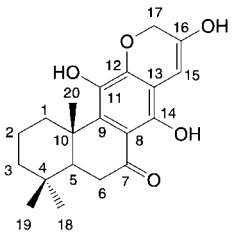
by **Hui Dou**[a]), **Xun Liao**[a]), **Shu-Lin Peng**[a]), **Yuan-Jiang Pan**[b]), and **Li-Sheng Ding***[a])

[a]) Chengdu Institute of Biology, Chinese Academy of Sciences, Chengdu 610041, P. R. China
[b]) Department of Chemistry, Zhejiang University, Hangzhou 310027 P.R. China
(fax: +86-28-8522-3843; e-mail: lsding@cib.ac.cn)

The new rearranged-abietane diterpene **1**, the four new triterpenoids **2**–**5**, and the new aminoethylphenyl oligoglycoside **6**, besides 19 known compounds, were isolated from the roots of *Schnabelia tetradonta*, a Chinese endemic herb. The structures of the new compounds were elucidated on the basis of spectroscopic evidence as 12,17-epoxy-11,14,16-trihydroxy-17(15 → 16)-*abeo*-abieta-8,11,13,15-tetraen-7-one (**1**), 21*β*-(*β*-D-glucopyranosyloxy)-2*α*,3*α*-dihydroxyolean-12-en-28-oic acid (**2**), 2*β*,3*β*,16*β*-trihydroxy-15-oxo-28-norolean-12-en-23-oic acid (**3**), 3*β*-[(4-*O*-acetyl-*β*-D-glucopyranuronosyl)oxy]-2*β*,16*β*-dihydroxy-28-norolean-15-oxo-12-en-23-oic acid (**4**), 3*β*-[(4-*O*-acetyl-6-*O*-methyl-*β*-D-glucopyranuronosyl)oxy]-2*β*,16*β*-dihydroxy-15-oxo-28-norolean-12-en-23-oic acid (**5**), and 4-[2-(acetylamino)ethyl]phenyl *O*-6-*O*-[(*Z*)-*p*-methoxycinnamoyl]-*β*-D-glucopyranosyl-(1 → 2)]-*O*-[*β*-D-glucopyranosyl-(1 → 3)]-4-*O*-acetyl-*α*-L-rhamnopyranoside (**6**), respectively.

Introduction. – The genus *Schnabelia* is distributed exclusively in China, and contains two species of plants, *S. oligophylla* and *S. tetradonta*. The latter, *S. tetradonta* (SUN) C. Y. WU et C. CHEN (Lamiaceae), commonly called 'Jin Gu Cao', is an endemic herbaceous plant used as a febrifuge to relieve internal fevers and as a remedy for rheumatism treatment in traditional Chinese medicine [1]. Up to date, there are few chemical constituents reported from this plant, except for our work dealing with some new compounds including three triterpenoids, an apigenin *C*-glycoside, an (aminoethyl)phenyl oligoglycoside, and a cyclopeptide from the aerial parts of *S. tetradonta* [2][3]. During our systematic chemical investigation of the EtOH extracts of the roots of *S. tetradonta*, the new rearranged-abietane diterpene **1**, the four new oleanane triterpenoids **2**–**5**, and the new (aminoethyl)phenyl oligoglycoside **6**, besides 19 known compounds, were isolated, the latter being teuvincenone F [4], 16-(*β*-D-glucopyranosyloxy)abieta-8,11,13-triene-11,12,19-triol [5], ajugaside A [5], oleanolic acid [6], epimaslinic acid [6], maslinic acid [6], 2*α*,3*α*,23,29-tetrahydroxyolean-12-en-28-oic acid [2], 2*β*,3*β*,19*α*-trihydroxyurs-12-en-28-oic acid [6], sitosterol [7], daucosterol [7], martynoside [8], isomartynoside [8], acetylmartynoside B [9], alyssonoside [10], leucosceptoside B [11], forsythoside B [12], amentoflavone [13], apigenin 6,8-di-*C*-*α*-L-arabinopyranoside [14] and 4-[2-(acetylamino)ethyl]phenyl *O*-6-*O*-[(*Z*)-*p*-methoxycinnamoyl]-*β*-D-glucopyranosyl-(1 → 2)]-*O*-[*β*-D-glucopyranosyl-(1 → 3)]-*α*-L-rhamnopyranoside (**8**) [2] were isolated. This paper deals with the isolation and structural elucidation of the six new compounds.

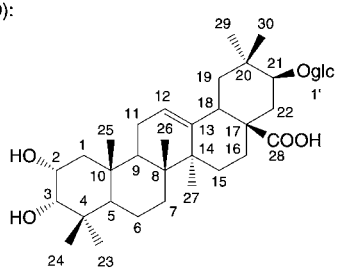
Results and Discussion. – Compound **1** was isolated as light yellow needles. The molecular formula ($C_{20}H_{24}O_5$) was obtained from the HR-FAB-MS showing the $[M+H]^+$ ion at *m/z* 345.1717. The IR spectrum exhibited the characteristic bands for OH



1

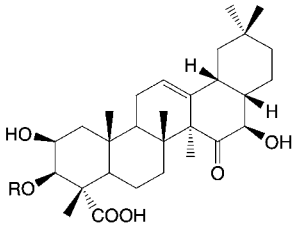
HMBC correlations (in (D_6) DMSO):
Me(18), Me(19)/C(4), C(5)
Me(20)/C(10)
H-C(5)/C(7), C(9)
CH_2(6)/C(7), C(8)
OH-C(11)/C(9), C(11), C(12)
OH-C(14)/C(8), C(13), C(14)
H-C(15)/C(12), C(13), C(16)
OH-C(16)/C(16)
CH_2(17)/C(12), C(15)

^{1}H,^{1}H COSY (in CD_3OD)
CH_2(2)/CH_2(1), CH_2(3)
H-C(5)/CH_2(6)

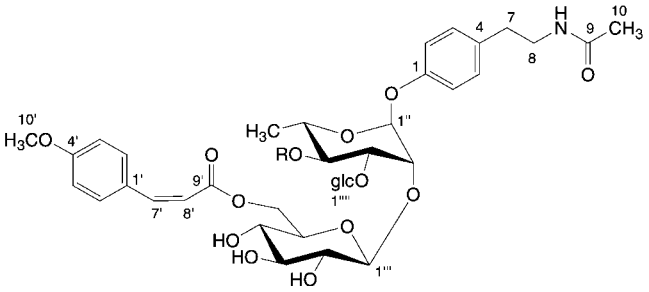


HMBC correlations:
H-C(3)/C(1), C(2), C(4), C(24)
Me(23), Me(24)/C(3), C(4), C(5)
Me(25)/C(9), C(10)
Me(26)/C(8), C(9), C(14)
Me(27)/C(13), C(14), C(15)
Me(29), Me(30)/C(19), C(20), C(21)
H-C(1')/C(21)

2



3 R = H
4 R = 4-*O*-acetylglucopyranuronosyl
5 R = 4-*O*-acetyl-6-*O*-methylglucopyranuronosyl
7 R = glucopyranuronosyl



6 R = Ac (arbitrary numbering)
8 R = H

(3449 cm^{-1}) and CO (1640 cm^{-1}) groups and an aromatic ring (1586 cm^{-1}). The ^{1}H- and ^{13}C-NMR data (*Table 1*) and 2D NMR experiments including ^{1}H,^{1}H COSY, HMQC, and HMBC suggested the structure 12,17-epoxy-11,14,16-trihydroxy-17(15 → 16)-*abeo*-abieta-8,11,13,15-tetraen-7-one for **1**.

Table 1. *^{1}H- and ^{13}C-NMR Data of* **1**. δ in ppm, J in Hz. Trivial numbering.

	In (D_6) DMSO		In CD_3OD	
	δ(C)	δ(H)	δ(C)	δ(H)
CH_2(1)	40.6		40.9	1.43 (*m*), 1.25 (*dt*, *J* = 13.6, 4.2)
CH_2(2)	18.6		18.9	1.70 (*m*), 1.54 (m)
CH_2(3)	36.3		36.4	3.42 (br. *d*, *J* = 10.8), 1.38 (*m*)
C(4)	40.4	–	40.6	–
H–C(5)	49.7	1.75 (*dd*, *J* = 14.7, 2.2)	49.8	1.80 (*dd*, *J* = 8.2, 4.8)
CH_2(6)	35.4	2.48 (*m*), 2.77 (*m*)	35.5	2.57 (*m*)
C(7)	206.1	–	205.6	–
C(8)	110.3	–	110.7	–
C(9)	135.3	–	134.9	–
C(10)	33.1	–	33.2	–
OH–C(11)	132.6	9.21[a]) (*s*)	132.6	–
C(12)	158.1	–	155.9	–
C(13)	115.9	–	116.0	–
OH–C(14)	152.2	13.78 (*s*)	152.6	–
H–C(15)	101.6	6.79 (*s*)	102.6	6.73 (*s*)
OH–C(16)	151.4	9.20[a]) (*s*)	151.5	–
CH_2(17)	55.9	4.54 (*s*)	56.5	4.62 (*s*)
Me(18)	32.9	0.91[b]) (*s*)	32.8	0.92[c]) (*s*)
Me(19)	17.9	1.36 (*s*)	17.9	1.38 (*s*)
Me(20)	21.4	0.92[b]) (*s*)	21.3	0.93[c]) (*s*)

[a]) [b]) [c]) Attributions with the same footnote may be interchanged.

The ^{1}H-NMR spectrum ((D$_6$)DMSO) of **1** exhibited 3*s* due to Me groups (δ 0.91, 0.92, 1.36), 2*s* due to an oxymethylene group (δ 4.54), and one low-field methine signal (δ 6.79), besides 3*s* for OH groups (δ 9.20, 9.21, 13.78). The ^{13}C-NMR spectrum showed signals of 8 aromatic C-atoms (δ 101.6–158.1) and of a keto function (δ 206.1), in addition to 11 upfield signals of saturated C-atoms (δ 17.9–55.9), suggesting a rearranged abietane skeleton [15]. The carbonyl group at C(7) was revealed by the correlations of H–C(5) (δ 1.75) and H–C(6) (δ 2.48, 2.77) with C(7) (δ 206.1) in the HMBC experiment. The structure of the rearranged abietane portion was established from the correlations of H–C(15) (δ 6.79) with C(12) (δ 158.1), C(13) (δ 115.9), and C(16) (δ 151.4) and from the correlations of 2 H–C(17) (δ 4.54) with C(12) (δ 158.1) and C(15) (δ 101.6) in the HMBC spectrum.

Compound **2** was isolated as white powder. The molecular formula ($C_{36}H_{58}O_{10}$) was obtained from the HR-FAB-MS showing the $[M-H]^-$ ion at *m/z* 649.3914. The IR spectrum exhibited the characteristic bands for OH (3428 cm^{-1}), CO (1732 cm^{-1}), and C=C (1648 cm^{-1}) groups. The presence of a D-glucose unit was established by the ^{13}C-NMR data (*Table 2*), and also by comparison with the authentic sample on TLC upon acid hydrolysis. The ^{1}H- (*Table 2*) and ^{13}C-NMR spectra as well as ^{1}H,^{1}H-COSY, HMQC, and HMBC experiments suggested the structure 21β-(β-D-glucopyranosyloxy)-2α,3α-dihydroxyolean-12-en-28-oic acid for **2**.

The ^{1}H-NMR spectrum of **2** showed an anomeric signal at δ 5.03 (*d*, *J* = 7.8 Hz) with a large coupling constant, suggesting the β-D-configuration of the glucose unit. In addition, ^{1}H- and ^{13}C-NMR spectra indicated the presence of an olean-12-ene type aglycone [2], containing 7 tertiary Me groups (δ 1.25, 0.86, 0.92, 0.95, 1.12, 1.35, 1.19), 1 carboxy group (δ 179.0), and 3 oxymethine C-atoms (δ 66.1, 79.3, 82.9). By comparison of the ^{13}C-NMR data of the aglycone of **2** with those of thomandertriol [16] and anchusoside IX [17], the same A-ring moiety as the former and the same E-ring moiety as the latter could be assigned to **2**. Therefore, the 2 OH groups

Table 2. *^{13}C-NMR Data* (C_5D_5N) *of* **2**–**5**. δ in ppm.

	2	**3**	**4**	**5**		**2**	**3**	**4**	**5**
C(1)	42.7	45.3	44.4	44.5	C(21)	82.9	34.6	34.5	34.5
C(2)	66.1	71.7	70.d	70.6	C(22)	40.3	20.7	20.6	20.6
C(3)	79.3	75.9	86.4	86.4	C(23)	29.3[a])	181.0	180.3	180.3
C(4)	38.6[b])	53.9	52.8	52.8	C(24)	22.2	13.9	14.1	14.0
C(5)	48.7	52.2	52.3	52.4	C(25)	16.5	17.3	17.0	17.0
C(6)	18.4	21.8	21.2	21.2	C(26)	17.4	18.2	18.1	18.1
C(7)	33.2	36.3	36.1	36.1	C(27)	26.0	20.6	20.5	20.6
C(8)	39.9	42.2	41.6	41.6	C(28)	179.0	–	–	–
C(9)	47.9	48.0	47.7	47.8	C(29)	29.4[a])	33.3	33.2	33.2
C(10)	38.8[b])	37.1	36.9	36.9	C(30)	18.4	23.3	23.2	23.2
C(11)	23.8	24.1	23.9	23.9	C(1′)	106.5	–	105.7	106.0
C(12)	122.8	125.3	125.1	125.1	C(2′)	75.7	–	72.6	72.4
C(13)	143.9	142.3	142.2	142.3	C(3′)	78.7	–	78.3	78.0
C(14)	42.2	54.7	54.6	54.6	C(4′)	71.7	–	71.2	70.9
C(15)	28.2	214.8	214.6	214.7	C(5′)	78.1	–	77.1	76.5
C(16)	24.9	76.1	76.0	76.0	C(6′)	62.9	–	172.2	170.1[c])
C(17)	48.6	44.2	44.1	44.1	Me*C*	–	–	170.6	170.5[c])
C(18)	41.4	46.0	45.8	45.8	*MeC*	–	–	21.0	21.0
C(19)	47.4	47.0	46.8	46.8	MeO	–	–	–	52.1
C(20)	37.0	31.0	30.9	30.9					

[a]) [b]) [c]) Attributions with the same footnote may be interchanged.

were α-positioned at C(2) and C(3), and the glucosyloxy group was located in β-position at C(21). HMBC Correlations of H–C(3) (δ 3.74, *d*, $J = 2.5$ Hz) with C(1) (δ 42.7), C(2) (δ 66.1), and C(4) (δ 38.6) confirmed the presence of OH at C(2) and C(3), their *cis*-configuration being indicated by the small coupling constant for H–C(3). The glucose unit was attached to C(21), as evidenced by HMBC correlations of C(21) (δ 82.9) with 2 H–C(22) (δ 2.24, 2.67), Me(29) (δ 1.35), Me(30) (δ 1.19), and H–C(1′) (δ 5.03), and its β-equatorial configuration was indicated by the *t* for H_β–C(22) (δ 2.24, *t*, $J = 12.8$ Hz).

Compound **3** was obtained as white needles. The HR-FAB-MS showed the $[M+H]^+$ ion at *m/z* 489.3183, indicating the molecular formula $C_{29}H_{44}O_6$. The IR spectrum exhibited absorptions indicative of OH (3451 cm^{-1}) and CO (1704 cm^{-1}) groups. The assignments of the ^{1}H- (*Table 3*) and ^{13}C-NMR data (*Table 2*) were made by comparison with those of compound **7** [2] and confirmed by HMBC and NOESY experiments. Thus, the structure of **3** was elucidated as 2β,3β,16β-trihydroxy-15-oxo-28-norolean-12-en-23-oic acid.

All ^{13}C-NMR signals of **3** were similar to those of **7** [2], except for the disappearance of the signals of the glucuronic acid unit and the significant upfield shift of C(3) (δ 75.9). The β-positioned OH–C(3) was confirmed by the HMBC correlations of H–C(3) (δ 4.76) and Me(24) (δ 2.07) with C(23) (δ 181.0) together with the NOESY correlation of H–C(3) (δ 4.76) with H–C(5) (δ 2.21). Therefore, **3** was suggested to be the aglycone of **7**.

Compound **4** was isolated as white needles. The molecular formula ($C_{37}H_{54}O_{13}$) was obtained from the HR-FAB-MS showing the $[M-H]^-$ ion at *m/z* 705.3509. Spectroscopically, **4** was similar to **7**, and readily identified as its C(4′) acetate [2].

The ^{1}H-NMR spectrum of **4** revealed both a characteristic *Me*CO signal (δ 1.99) and significant deshielding of H–C(4′) (δ 5.83) (*Table 3*) compared to the corresponding ^{1}H-NMR data of **7** (δ 4.50). The correlations

Table 3. *^{1}H-NMR Data* (C_5D_5N) *of* **2**–**5**. δ in ppm, J in Hz.

	2	**3**	**4**	**5**
CH_2 (1)	1.78 (*m*), 1.86 (m)			
H–C(2)	4.28 (*m*)	4.62 (*m*)	4.84 (*m*)	4.79 (*m*)
H–C(3)	3.74 (*d*, J = 2.5)	4.76 (*d*, J = 4.0)	4.70 (*d*, J = 3.6)	4.69 (*d*, J = 3.8)
H–C(5)	1.61 (br. *d*, J = 11.5)	2.21 (*m*)	2.13 (*m*)	2.13 (*m*)
CH_2(6)	1.09 (*m*)			
CH_2(7)	1.27 (*m*)			
H–C(9)	1.88 (*m*)			
CH_2(11)	1.95 (*m*)			
H–C(12)	5.46 (br. *s*)	5.49 (br. *s*)	5.43 (br. *s*)	5.43 (br. *s*)
CH_2(15)	1.08 (*m*)	–	–	–
CH_2(16) or H–C(16)	2.09 (*m*)	4.46 (br. *s*)	4.47 (br. *s*)	4.48 (br. *s*)
H–C(17)	–	2.67 (*m*)	2.64 (*m*)	2.63 (*m*)
H–C(18)	3.35 (*dd*, J = 14.1, 4.0)	2.88 (*m*)	2.84 (*dd*, J = 14.2, 3.8)	2.82 (br. *d*, J = 14.1)
CH_2(19)	1.37 (*m*), 1.97 (*m*)			
H–C(21) or CH_2(21)	4.00 (*m*)			
H_β–C(22)	2.24 (*t*, J = 12.8)			
H_α–C(22)	2.67 (*dd*, J = 12.8, 4.4)			
Me(23) or C(23)	1.25 (*s*)	–	–	–
Me(24)	0.86 (*s*)	2.07 (*s*)	2.00 (*s*)	2.00 (*s*)
Me(25)	0.92 (*s*)	1.73 (*s*)	1.63 (*s*)	1.64 (*s*)
Me(26)	0.95 (*s*)	1.23 (*s*)	1.19 (*s*)	1.19 (*s*)
Me(27)	1.12 (*s*)	1.25 (*s*)	1.22 (*s*)	1.22 (*s*)
Me(29)	1.35 (*s*)	0.79 (*s*)	0.77 (*s*)	0.77 (*s*)
Me(30)	1.19 (*s*)	0.85 (*s*)	0.83 (*s*)	0.83 (*s*)
H–C(1′)	5.03 (*d*, J = 7.8)	–	5.26 (*d*, J = 7.6)	5.24 (*d*, J = 7.8)
H–C(2′)	4.02 (*m*)	–	3.98 (*m*)	3.90 (*m*)
H–C(3′)	4.27 (*m*)	–	4.52 (*t*, J = 9.5)	4.36 (*t*, J = 9.6)
H–C(4′)	4.26 (*m*)	–	5.83 (*t*, J = 9.5.)	5.73 (*t*, J = 9.6)
H–C(5′)	4.04 (*m*)	–	4.64 (*d*, J = 9.5)	4.55 (*d*, J = 9.6)
CH_2(6′)	4.37 (*dd*, J = 11.6, 5.0), 4.54 (*dd*, J = 11.6, 2.4)	–	–	–
AcO	–	–	1.99 (*s*)	1.97 (*s*)
MeO	–	–	–	3.65 (*s*)

observed in the HMBC experiment of H–C(4′) with Me*C*O (δ 170.6) and C(2′) (δ 72.6) confirmed the above described deduction.

Compound **5** was isolated as white needles. The molecular formula ($C_{38}H_{56}O_{13}$) was established by the HR-FAB-MS exhibiting $[M-H]^-$ at *m/z* 719.3664. The ^{1}H- and ^{13}C-NMR spectra differed from those of **4** only by an extra MeO signal (δ(H) 3.65, δ(C) 52.1) and the upfield shift of C(6′) (δ 170.1) (*Tables 2* and *3*), suggesting the esterification at C(6′) of the glucuronic acid unit. This was substantiated by the correlation of the MeO group (δ 3.65) with C(6′) (δ 170.1) in the HMBC experiment.

Compound **6** was obtained as white needles. The molecular formula ($C_{40}H_{53}NO_{19}$) was established by the $[M-H]^-$ ion at *m/z* 851.3156 in the HR-FAB-MS. The IR spectrum of **6** exhibited absorptions indicative of OH (3370 cm^{-1}) and ester CO

(1713 cm^{-1}) groups and aromatic rings (1604, 1512 cm^{-1}). The assignments of the ^1H- and ^{13}C-NMR data (*Table 4*) were made by comparison with those of compound **8** [2] and confirmed by HMQC and HMBC experiments. Thus, the structure of **6** was elucidated as 4-[2-(acetylamino)ethyl]phenyl *O*-6-*O*-[(*Z*)-*p*-methoxycinn amoyl]-β-D-glucopyranosyl-(1 → 2)-*O*-[β-D-glucopyranosyl-(1 → 3)]-4-*O*-acetyl-α-L-rhamnopyranoside.

Table 4. *^1H- and ^{13}C-NMR* (C_5D_5N) *Data of* **6**. δ in ppm, *J* in Hz. Arbitrary numbering.

	δ(C)	δ(H)		δ(C)	δ(H)
C(1)	155.3	–	H–C(3″)	80.0	5.04 (*m*)
H–C(2), H–C(6)	117.0	7.17 (*s*)	H–C(4″)	72.9	5.76 (*m*)
H–C(3), H–C(5)	130.3	7.17 (*s*)	H–C(5″)	67.7	4.14 (*m*)
C(4)	133.9	–	Me(6″)	17.8	1.13 (*d*, *J* = 6.1)
CH_2(7)	35.4	2.85 (*t*, *J* = 7.2)			
CH_2(8)	41.4	3.61 (*t*, *J* = 7.2)	*Glc:*		
NH	–	8.51 (*t*, *J* = 5.8)	H–C(1‴)	106.2	5.09 (*d*, *J* = 7.5)
C(9)	169.9	–	H–C(2‴)	75.2	4.04 (*m*)
Me(10)	23.0	2.02 (*s*)	H–C(3‴)	78.1[a])	4.18 (*m*)
C(1′)	127.8	–	H–C(4‴)	71.2	4.03 (*m*)
H–C(2′), H–C(6′)	133.2	7.95 (*d*, *J* = 8.9)	H–C(5‴)	74.8	3.97 (*m*)
H–C(3′), H–C(5′)	113.9	6.94 (*d*, *J* = 8.9)	CH_2(6‴)	64.4	4.69 (*dd*, *J* = 11.7, 5.6), 5.04 (*m*)
C(4′)	161.0	–			
H–C(7′)	143.7	6.77 (*d*, *J* = 13.0)	*Glc:*		
H–C(8′)	116.9	5.76 (*d*, *J* = 13.0)	H–C(1⁗)	106.5	5.36 (*d*, *J* = 7.5)
C(9′)	166.5	–	H–C(2⁗)	75.2	4.04 (*m*)
Me(10′)	55.2	3.66 (*s*)	H–C(3⁗)	77.9[a])	4.16 (*m*)
			H–C(4⁗)	70.9	4.16 (*m*)
Rha:			H–C(5⁗)	78.5[b])	4.06 (*m*)
H–C(1″)	98.6	6.33 (*d*, *J* = 1.1)	CH_2(6⁗)	62.3	4.33 (*m*), 4.40 (*m*)
H–C(2″)	78.6[b])	4.79 (*dd*, *J* = 10.0, 3.5)	MeCO	170.5	–
H–C(3″)	80.0	5.04 (*m*)	*Me*CO	21.1	2.23 (*s*)

[a]) [b]) Attributions with the same footnote may be interchanged.

The ^1H- and ^{13}C-NMR spectra of **6** are similar to those of compound **8** [2]. The appearance of an additional *Me*CO signal (δ 2.23) suggested that **6** was a monoacetylated derivative of **8**. The significant deshielding of H–C(4″) (δ 5.76) compared to the corresponding ^1H-NMR data for **8** (δ 4.36) and the HMBC correlations of H–C(4″) with Me*C*O (δ 170.5) and C(6″) (δ 17.8) showed that the MeCOO group was located at C(4″) of the rhamnose unit.

Experimental Part

General. Column chromatography (CC): silica gel (160–200 mesh; *Qingdao Marine Chemical Group Co.*), *MCI-CHP-20* gel (75–150 μm; *Mitsubishi Chemical Corporation*), *ODS* (*Cosmosil 75C_{18}-OPN*; *Nacalai tesque*), and *Lobar LiChroprep RP-18* (40–68 μm; *Merck*). M.p.: *XRC-1* apparatus; uncorrected. Optical rotations: *Perkin-Elmer 241* polarimeter. IR Spectra: *Nicolet MX-1* spectrometer. NMR Spectra: *Bruker AM-400* spectrometer; $SiMe_4$ as internal standard. MS: for HR-FAB; *VG-AutoSpec 3000* spectrometer; for ESI, *Finnigan LCQ^{DECA}* spectrometer, in *m/z*.

Plant Material. The plants of *S. tetradonta* were collected from Yibin, Sichuan, China, in August 2000 and identified by Prof. *Liu Zheng-Yu* and Prof. *Zhao Zuo-Cheng*. A voucher specimen (No. 20000825) was deposited in the herbarium of Chengdu Institute of Biology, Chinese Academy of Sciences.

Extraction and Isolation. Dried and powdered roots of *S. tetradonta* (15 kg) were extracted with 95% EtOH at r.t. (3×10 days) to give an extract (1.2 kg), which was suspended in H_2O and extracted successively with petroleum ether, AcOEt, and BuOH. The AcOEt extract (75 g) was separated by CC (*MCI CHP-20*, MeOH/H_2O 6:4 → 9:1): *Fr. I–III*. *Fr. I* (50 g) was subjected to CC (silica gel, petroleum ether/acetone 10:1 → 1:2): *Fr. I.1–I.8*. *Fr. I.3* (830 mg) on CC (silica gel, $CHCl_3$/MeOH 30:1 → 10:1) gave 2*β*,3*β*,19*α*-trihydroxyurs-12-en-28-oic acid (24 mg). *Fr. I.4* (9.1 g) on CC (silica gel, $CHCl_3$/MeOH 30:1 → 8:1) gave acetylmartynoside B (220 mg), 2*α*,3*α*,23,29-tetrahydroxyolean-12-en-28-oic acid (30 mg) after further purification on CC (*ODS,* MeOH/H_2O 4:6 → 6:4) and amentoflavone (14 mg). *Fr. I.5* (9.5 g) was subjected to CC (silica gel, $CHCl_3$/MeOH 30:1 → 7:1): *Fr. I.5a–I.5g.* Compounds **5** (11 mg) and **4** (35 mg) were obtained from *Fr. I.5b* (1 g) and *Fr. I.5d* (2.1 g), resp., after purification on CC (*ODS,* MeOH/H_2O 6:4, 7:3). *Fr. I.5e* (1 g) on CC (*ODS,* MeOH/H_2O 5:5–8:2) gave 16-(*β*-D-glucopyranosyloxy)abieta-8,11,13-triene-11,12,19-triol (140 mg). *Fr. I.5f* (1.1 g) on CC (*ODS,* MeOH/H_2O 4:6, 5:5) gave **2** (4 mg) and martynoside (380 mg). *Fr. II* (9.4 g) was subjected to CC (silica gel, $CHCl_3$, then $CHCl_3$/MeOH 40:1 → 10:1): *Fr. II.1–II.8. Fr. II.5* (3.1 g) on CC (silica gel, petroleum ether/acetone 10:1 → 3:1) gave oleanolic acid (9 mg), epimaslinic acid (70 mg), **1** (190 mg), and teuvincenone F (80 mg). *Fr. II.6* (1 g) on CC (silica gel, petroleum ether/acetone 10:1) gave maslinic acid (80 mg). Compound **3** (4 mg) and sitosterol (360 mg) were obtained from *Fr. II.8* (600 mg) and *Fr. III* (1.2 g) resp., by crystallization. The BuOH extract (160 g) was separated by CC (silica gel, CH_3Cl/MeOH 20:1 → 1:1): *Fr. I–IX.* Daucosterol (2.7 g) was obtained from *Fr. I* (5.7 g) by crystallization. *Fr. II* (5.2 g) on CC (silica gel, $CHCl_3$/MeOH 8:1) gave martynoside (100 mg) and isomartynoside (21 mg), resp., after purification on CC (*ODS,* MeOH/H_2O 4:6 → 6:4). *Fr. III* (4.8 g) on CC (silica gel, $CHCl_3$/MeOH 8:1; then *ODS,* MeOH/H_2O 3:7 → 6:4) gave **8** (8 mg). *Fr. IV* (12.6 g) on CC (silica gel, $CHCl_3$/MeOH 6:1) gave leucosceptoside B (6.4 g) and **6** (160 mg), the latter after purification on CC (*Lobar LiChroprep RP-18*, MeOH/H_2O 5:5). *Fr. V* (6 g) on CC (silica gel, $CHCl_3$/MeOH 5:1) gave ajugaside A (120 mg). Alyssonoside (2.2 g) was obtained from *Fr. VI* (13.1 g) on CC (silica gel, $CHCl_3$/MeOH 5:1; then *ODS*, MeOH/H_2O 2:8 → 4:6). Apigenin 6,8-di-*C*-*α*-L-arabinopyranoside (580 mg) was obtained from *Fr. VII* (11 g) on CC (silica gel, $CHCl_3$/MeOH 4:1; then *ODS*, MeOH/H_2O 4:6, 5:5). Forsythoside B (30 g) was obtained from *Fr. IX* (40 g) on CC (silica gel, $CHCl_3$/MeOH 2:1; then *ODS*, MeOH/H_2O 3:7, 4:6).

12,17-Epoxy-11,14,16-trihydroxy-17(15 → 16)-abeo-*abieta-8,11,13,15-tetraen-7-one* (=*(4a*S*,12b*S*)-1,2,3,4,4a,5,10,12b-Octahydro-7,9,12-trihydroxy-4,4,12b-trimethyl-6*H*-phenanthro[3,2-*b*]pyran-6-one*; **1**). Light yellow needles (190 mg). M.p. 254–256° (MeOH). $[\alpha]_D^{20} = +127.5$ ($c = 0.120$, MeOH). IR (KBr): 3449, 2925, 1630, 1586, 1456, 1371, 1269, 1211, 1073, 817, 785, 604. ^{1}H- and ^{13}C-NMR: *Table 1*. HR-FAB-MS: 345.1717 ($C_{20}H_{25}O_5^+$; calc. 345.1702).

*(2α,3α,21β)-21-(β-*D*-Glucopyranosyloxy)-2,3-dihydroxyolean-12-en-28-oic Acid* (**2**). White powder (4 mg). $[\alpha]_D^{20} = +12.8$ ($c = 0.195$, MeOH). IR (KBr): 3429, 2952, 1732, 1694, 1648, 1459, 1386, 1076, 1027. ^{1}H-NMR: *Table 3*. ^{13}C-NMR: *Table 2*. HR-FAB-MS: 649.3914 ($C_{36}H_{57}O_{10}^-$; calc. 649.3952).

(2β,3β,4α,16β)-2,3,16-Trihydroxy-15-oxo-28-norolean-12-en-23-oic Acid (**3**). White needles (4 mg). M.p. > 350° (MeOH). $[\alpha]_D^{20} = +36.4$ ($c = 0.109$, MeOH). IR (KBr): 3451, 2943, 1704, 1634, 1456, 1394, 1307, 1258, 1149, 1053, 973. ^{1}H-NMR: *Table 3*. ^{13}C-NMR: *Table 2*. HR-FAB-MS: 489.3183 ($C_{29}H_{45}O_6^+$; calc. 489.3216).

*(2β,3β,4α,16β)-3-[(4-*O*-Acetyl-β-*D*-glucopyranuronosyl)oxy]-2,16-dihydroxy-15-oxo-28-norolean-12-en-23-oic Acid* (**4**). White needles (35 mg). M.p. > 350° (MeOH). $[\alpha]_D^{20} = +24.9$ ($c = 0.140$, MeOH). IR (KBr): 3484, 2932, 1722, 1707, 1640, 1382, 1249, 1029. ^{1}H-NMR: *Table 3*. ^{13}C-NMR: *Table 2*. HR-FAB-MS: 705.3509 ($C_{37}H_{53}O_{13}^-$; calc. 705.3486).

*(2β,3β,4α,16β)-3-[(4-*O*-Acetyl-6-*O*-methyl-β-*D*-glucopyranuronosyl)oxy]-2,16-dihydroxy-15-oxo-28-norolean-12-en-23-oic Acid* (**5**). White needles (11 mg). M.p. 254–256° (MeOH). $[\alpha]_D^{20} = +55.6$ ($c = 0.090$, MeOH). IR (KBr): 3467, 2951, 1731, 1704, 1552, 1383, 1251, 1029, 972. ^{1}H-NMR: *Table 3*. ^{13}C-NMR: *Table 2*. HR-FAB-MS: 719.3664 ($C_{38}H_{55}O_{13}^-$; calc. 719.3643).

4-[2-(Acetylamino)ethyl]phenyl O-*6*-O-*[(2*Z*)-3-(4-Methoxyphenyl)-1-oxoprop-2-enyl]-β-*D*-glucopyranosyl-(1 → 2)*-O-*[β-*D*-glucopyranosyl(1 → 3)]-4-*O-*acetyl-6-deoxy-α*-L*-mannopyranoside* (**6**). White needles (160 mg). M.p. 156–158° (MeOH). $[\alpha]_D^{20} = -16.4$ ($c = 0.195$, MeOH). IR (KBr): 3370, 2922, 1713, 1636, 1604, 1512, 1379, 1229, 1168, 1079, 1037, 829. ^{1}H- and ^{13}C-NMR: *Table 4*. HR-FAB-MS: 851.3156 ($C_{40}H_{53}NO_{19}^-$ calc. 851.3212).

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