Triterpenoid Saponins from *Schefflera arboricola*

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Four new triterpenoid saponins, named scheffarboside A – D (**1**–**4**), along with five known saponins were isolated from the stems of *Schefflera arboricola*. The structures of the four new saponins were determined as 3-*O*-(*O*-*β*-glucuronopyranosyl-(1 → 3)-*O*-*α*-rhamnopyranosyl-(1 → 2)-*α*-arabinopyranosyl)-oleanolic acid (**1**), 3-*O*-(*O*-*α*-arabinopyranosyl-(1 → 4)-*O*-*α*-arabinopyranosyl-(1 → 3)-*O*-*α*-rhamnopyranosyl-(1 → 2)-*α*-arabinopyranosyl)oleanolic acid (**2**), 3-*O*-(*O*-*α*-arabinopyranosyl-(1 → 4)-*O*-*α*-arabinopyranosyl-(1 → 3)-*O*-*α*-rhamnopyranosyl-(1 → 2)-*α*-arabinopyranosyl)hederagenin (**3**), 3-*O*-(*O*-*α*-arabinopyranosyl-(1 → 4)-*O*-*α*-arabinopyranosyl-(1 → 3)-*O*-*α*-rhamnopyranosyl-(1 → 2)-*α*-arabinopyranosyl)oleanolic acid *O*-*α*-rhamnopyranosyl-(1 → 4)-*O*-*β*-glucopyranosyl-(1 → 6)-*β*-glucopyranosyl-ester (**4**), respectively, on the basis of spectroscopic and chemical degradation methods.

Introduction. – Several plants of the *Schefflera* genus (Araliaceae) are used as folk remedies for the treatment of pain, rheumatic arthritis, fracture, and sprain in China [1]. A series of triterpenoids and triterpenoid glycosides were isolated from this genus [2–5]. In our chemical investigation on *S. arboricola*, four new triterpenoid saponins, named scheffarboside A–D (**1**–**4**) and five known ones, quinatoside A, hederagenin[1]) 3-(*α*-L-arabinopyranoside), eleutheroside K, CP_3, and sieboldianoside A, were isolated from the stems of *S. arboricola*. Herein, we report the isolation and structure determination of the four new compounds **1**–**4**.

Results and Discussion. – Compound **1** was obtained as white amorphous powder. In the IR spectrum, absorption bands at 3421 (OH) and 1693 cm^{-1} (COOH) were apparent. The molecular formula $C_{47}H_{74}O_{17}$ was determined by HR-ESI-MS (*m*/*z* 933.4855, $[M+Na]^+$). Acid hydrolysis of **1** afforded oleanolic acid[1]) and arabinose, rhamnose (=6-deoxymannose), and glucuronic acid as the sugar components detected by co-TLC with authentic samples. The sequence of the three sugar moieties was deduced by ESI-MS-MS of **1**, which exhibited a $[M-H]^-$ peak at *m*/*z* 909 and fragments at *m*/*z* 733 ($[M-H-GluA]^-$), 587 ($[M-H-GluA-Rha]^-$), and 455 ($[M-H-GluA-Rha-Ara]^-$). The ^{13}C-NMR (*Table 1*), ^{1}H-NMR (*Table 2*), ^{1}H,^{1}H-COSY, HSQC, and HMBC led to the assignment of all protons and C-atoms. Thus, the structure of **1** was concluded to be 3-*O*-(*O*-*β*-glucuronopyranosyl-(1 → 3)-*O*-*α*-rhamnopyranosyl-(1 → 2)-*α*-arabinopyranosyl)oleanolic acid[1]). Since this is a rare new triterpenoid sap-

[1]) Oleanolic acid = (3*β*)-3-hydroxyolean-12-en-28-oic acid; hederagenin = (3*β*,4*α*)-3,23-dihydroxyolean-12-en-28-oic acid.

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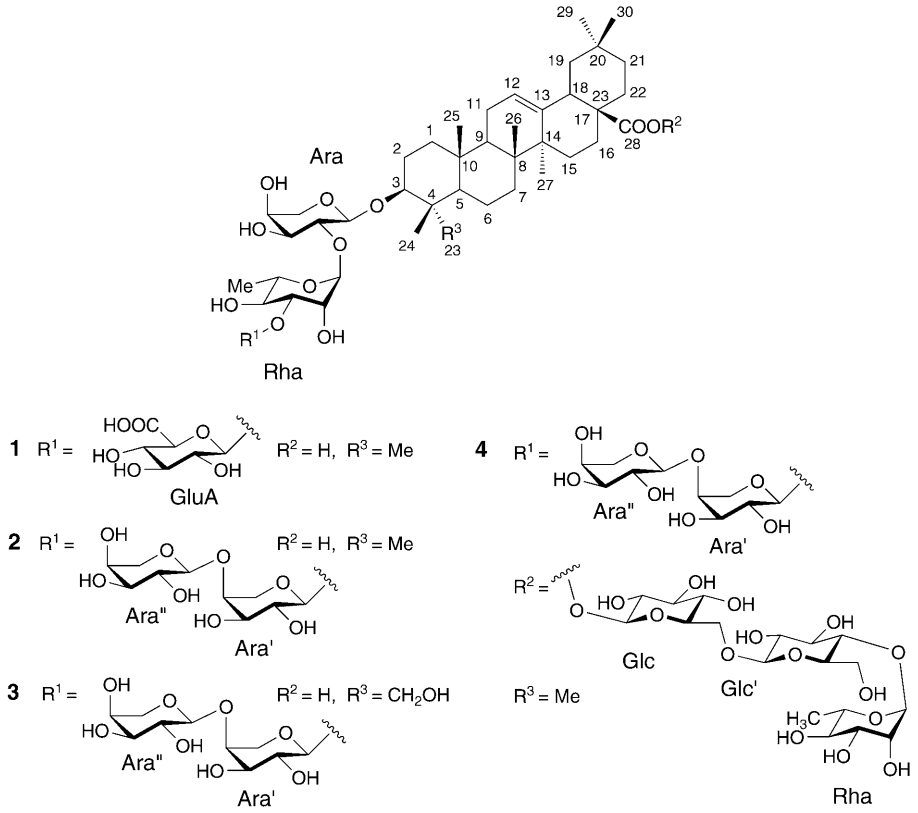

onin terminated with a glucuronic acid, it was assigned the trivial name scheffarboside A.

In the ^{1}H-NMR spectrum of **1** (*Table 2*), 6 Me-signals and an olefinic proton (H–C(12) at δ 5.40, br. *s*) were observed, which suggested that **1** is an oleanolic acid derivative. In the ^{13}C-NMR spectrum (*Table 1*), the signals due to the aglycone moiety were in good agreement with those of an oleanolic acid glycoside [6], while the signals for C(3) at δ 87.9 and C(28) at δ 180.2 established that **1** was a 3-*O*-glycosyl derivative. The proton system of each sugar unit was deduced by a ^{1}H,^{1}H-COSY experiment, and the connectivity of the ^{1}H- and ^{13}C-NMR signals was determined by the HSQC spectrum. The information concerning the sequence of the oligosaccharide chains and the linkage sites to the aglycone were obtained by HMBC analysis, in which the correlations of δ 4.78 (H–C(1′) of Ara) to δ 87.9 (C(3)), δ 6.04 (H–C(1″) of Rha) to δ 74.0 (C(2′) of Ara), and δ 5.07 (H–C(1‴) of GluA) to δ 82.2 (C(3″) of Rha) indicated that a GluA-(1 → 3)-Rha-(1 → 2)-Ara trisaccharide moiety was located at C(3) of oleanolic acid. Three anomeric proton signals at δ 6.04 (br. *s*), δ 5.07 (*d*, J = 8.0 Hz), and δ 4.78 (*d*, J = 5.5 Hz) in the ^{1}H-NMR spectrum indicated the rhamnose, glucuronic acid, and arabinose units to be in the α-, β- and α-glycosidic forms, respectively.

Scheffarboside B (**2**), a white amorphous powder, had a molecular formula $C_{51}H_{82}O_{19}$ as determined by HR-ESI-MS (*m*/*z* 1021.5300, $[M+Na]^+$). The IR spectrum showed the absorption bands of an OH (3419 cm^{-1}) and carboxyl group (1693 cm^{-1}). Acid hydrolysis of compound **2** afforded oleanolic acid as aglycone and rhamnose

Table 1. *^{13}C-NMR* (100 MHz) *Data of Saponins* **1**–**4** *in Pyridine.* δ in ppm.

	1[a])	**2**	**3**	**4**[a])		**1**[a])	**2**	**3**	**4**[a])	**4**[a])
C(1)	38.6	38.8	38.9	38.6						
C(2)	26.2	26.6	26.3	26.3		3-*O*-Ara	3-*O*-Ara	3-*O*-Ara	3-*O*-Ara	28-*O*-Glc
C(3)	87.9	88.6	81.0	88.5	C(1′)	104.3	105.2	104.6	104.8	95.2
C(4)	39.3	39.5	43.5	39.5	C(2′)	74.0	75.3	75.1	75.0	73.3
C(5)	55.6	55.9	47.6	55.7	C(3′)	72.7	74.5	75.1	73.7	77.9
C(6)	18.0	18.4	18.1	18.2	C(4′)	67.6	69.2	69.3	68.7	70.0
C(7)	32.7	33.1	32.8	32.1	C(5′)	64.4	65.5	66.2	65.0	77.5
C(8)	39.2	39.6	39.7	39.2	C(6′)					68.6
C(9)	47.6	48.0	48.1	47.8		Rha	Rha	Rha	Rha	Glc′
C(10)	36.6	37.0	36.8	36.7	C(1″)	101.3	101.5	101.3	100.9	104.1
C(11)	23.2	23.7	23.6	23.4	C(2″)	71.6	71.9	71.8	71.4	74.7
C(12)	122.2	122.5	122.4	122.5	C(3″)	82.2	82.9	82.9	82.0	76.0
C(13)	144.4	144.7	144.9	143.9	C(4″)	73.2	72.9	72.9	72.3	78.0
C(14)	41.7	42.1	42.1	41.8	C(5″)	69.6	69.6	69.4	69.3	76.6
C(15)	27.9	28.3	28.3	27.9	C(6″)	18.4	18.4	18.4	18.1	60.8
C(16)	23.2	23.7	23.7	23.0		GluA	Ara′	Ara′	Ara′	Rha
C(17)	46.3	46.6	46.6	45.9	C(1‴)	103.9	107.1	107.1	106.3	102.3
C(18)	41.5	41.9	41.9	41.3	C(2‴)	74.0	75.4	75.4	74.8	72.0
C(19)	46.1	46.4	46.4	45.9	C(3‴)	76.9	75.9	75.9	75.3	72.1
C(20)	30.5	30.9	30.9	30.4	C(4‴)	71.7	76.1	76.0	75.9	73.3
C(21)	33.8	34.2	34.2	33.6	C(5‴)	76.2	64.8	64.8	64.3	70.1
C(22)	32.7	33.1	33.2	32.7	C(6‴)	173.9				18.1
C(23)	27.7	28.1	63.8	27.8			Ara″	Ara″	Ara″	
C(24)	16.4	17.1	14.1	16.8	C(1⁗)		103.6	103.6	103.1	
C(25)	15.2	15.5	16.0	15.3	C(2⁗)		71.3	71.2	70.9	
C(26)	17.0	17.3	17.4	17.1	C(3⁗)		74.3	74.2	73.7	
C(27)	25.8	26.1	26.1	25.8	C(4⁗)		69.3	69.7	68.8	
C(28)	180.2	180.2	180.7	176.4	C(5⁗)		67.3	67.3	66.8	
C(29)	32.9	33.2	33.2	32.8						
C(30)	23.4	23.7	23.7	23.4						

[a]) Measured in C_5D_5N/D_2O.

and arabinose as sugar components. Compound **2** was concluded to be 3-*O*-(*O*-α-arabinopyranosyl-(1 → 4)-*O*-α-arabinopyranosyl-(1 → 3)-*O*-α-rhamnopyranosyl-(1 → 2)-α-arabinopyranosyl)oleanolic acid[1]).

The ^{13}C-NMR spectrum of **2** exhibited four anomeric signals at δ 107.1, 105.2, 103.6, and 101.5. The signals for C(3) at δ 88.6 and C(28) at δ 180.2 established that **2** was a 3-*O*-glycosyl derivative. The ^{1}H,^{1}H-COSY experiment allowed us to establish the proton sequence of the sugar fragment. The assignment of their corresponding C-atoms was made by a HSQC spectrum. The Ara-(1 → 4)-Ara-(1 → 3)-Rha-(1 → 2)-Ara saccharide moiety at C(3) of oleanolic acid was deduced from the HMBC correlations between C(3) (δ 88.6) and H–C(1′) of Ara (δ 4.83), between C(2′) of Ara (δ 75.3) and H–C(1″) of Rha (δ 6.21), between C(3″) of Rha (δ 82.9) and H–C(1‴) of Ara′ (δ 5.25), and between C(4‴) of Ara′ (δ 76.1) and H–C(1⁗) of Ara″ (δ 4.82). The above conclusion was also supported by the observed ROESY correlations: δ 4.83 (H–C(1′))/δ 3.28 (H–C(3)), δ 6.21 (H–C(1″))/δ 4.58 (H–C(2′)), δ 5.25 (H–C(1‴))/δ 4.67 (H–C(3″)), δ 4.82 (H–C(1⁗))/δ 4.32 (H–C(4‴)). The relative configuration of each monosaccharide was determined based on the characteristic J(1,2) coupling constant.

Table 2. *^{1}H-NMR* (400 MHz) *Data of Saponins* **1**–**4** *in Pyridine.* δ in ppm, J in Hz.

	1[a])	**2**[b])	**3**	**4**[a])[b])	**4**[a])[b])
H–C(3)	3.24 (br. *d*, *J* = 11.0)	3.28[c])	4.29[c])	3.27 (br. *d*, *J* = 11.0)	
H–C(12)	5.40 (br. *s*)	5.45 (br. *s*)	5.45 (br. *s*)	5.42 (br. *s*)	
Me(23) or CH_2(23)	1.13 (*s*)	1.27 (*s*)	4.28[c]), 3.89 (*d*, *J* = 10.2)	1.26 (*s*)	
Me(24)	1.03 (*s*)	1.11 (*s*)	1.12 (*s*)	1.11 (*s*)	
Me(25)	0.75 (*s*)	0.83 (*s*)	0.91 (*s*)	0.86 (*s*)	
Me(26)	0.88 (*s*)	0.96 (*s*)	0.98 (*s*)	1.06 (*s*)	
Me(27)	1.23 (*s*)	1.29 (*s*)	1.22 (*s*)	1.26 (*s*)	
Me(29)	0.89 (*s*)	0.95 (*s*)	0.89 (*s*)	0.91 (*s*)	
Me(30)	0.93 (*s*)	1.00 (*s*)	0.98 (*s*)	0.89 (*s*)	
	3-*O*-Ara	3-*O*-Ara	3-*O*-Ara	3-*O*-Ara	28-*O*-Glc
H–C(1′)	4.78 (*d*, *J* = 5.5)	4.83 (*d*, *J* = 6.4)	5.05 (*d*, *J* = 6.4)	4.85 (*d*, *J* = 6.0)	6.18 (*d*, *J* = 7.8)
H–C(2′)	4.54[c])	4.58 (*dd*, *J* = 6.8, 6.4)	4.59 (*dd*, *J* = 8.2, 6.4)	4.54 (*dd*, *J* = 9.3, 6.0)	4.12[c])
H–C(3′)	4.27[c])	4.23[c])	4.02 (*dd*, *J* = 8.2, 3.3)	4.24[c])	4.24 (*t*, *J* = 8.8)
H–C(4′)	4.52[c])	4.28 (*m*)	4.29 (*m*)	4.29 (*m*)	4.31[c])
CH_2(5′) or H–C(5′)	3.73 (br. *d*, *J* = 12.7), 4.19[c])	3.80 (br. *d*, *J* = 10.8), 4.30[c])	3.68 (br. *d*, *J* = 10.9), 4.25[c])	3.82 (br. *d*, *J* = 10.8), 4.31[c])	4.07[c])
CH_2(6′)					4.30[c]), 4.63[c])
	Rha	Rha	Rha	Rha	Glc′
H–C(1″)	6.04 (br. *s*)	6.21 (br. *s*)	6.35 (br. *s*)	6.15 (br. *s*)	4.96 (*d*, *J* = 7.8)
H–C(2″)	4.66 (br. *s*)	4.86 (br. *s*)	4.88 (br. *s*)	4.84 (br. *s*)	3.93 (*dd*, *J* = 9.3, 7.8)
H–C(3″)	4.26[c])	4.67 (*dd*, *J* = 9.3, 2.4)	4.71[c])	4.64[c])	4.08[c])
H–C(4″)	4.22[c])	4.44 (*t*, *J* = 9.3)	4.47 (*t*, *J* = 9.5)	4.44 (*t*, *J* = 9.3)	4.30[c])
H–C(5″)	4.50[c])	4.60 (*dq*, *J* = 9.3, 6.4)	4.71[c])	4.57 (*dq*, *J* = 9.3, 5.9)	3.59 (br. *d*, *J* = 9.8)
Me(6″) or CH_2(6″)	1.53 (*d*, *J* = 6.1)	1.53 (*d*, *J* = 6.4)	1.54 (*d*, *J* = 5.9)	1.54 (*d*, *J* = 5.9)	4.03[c]), 4.17[c])
	GluA	Ara′	Ara′	Ara′	Rha
H–C(1‴)	5.07 (*d*, *J* = 8.0)	5.25 (*d*, *J* = 7.8)	5.28 (*d*, *J* = 7.6)	5.21 (*d*, *J* = 7.8)	5.75 (br. *s*)
H–C(2‴)	3.95 (*t*, *J* = 8.4)	3.99 (*dd*, *J* = 8.8, 7.8)	4.01 (*dd*, *J* = 9.1, 7.6)	4.04 (*dd*, *J* = 8.8, 7.8)	4.64[c])
H–C(3‴)	4.20[c])	4.13[c])	4.12[c])	4.11[c])	4.51 (*dd*, *J* = 9.5, 3.2)
H–C(4‴)	4.52[c])	4.32 (*m*)	4.28 (*m*)	4.24 (*m*)	4.30[c])
H–C(5‴) or CH_2(5‴)	4.42 (*m*)	3.59 (br. *d*, *J* = 10.7), 4.38 (*m*)	3.58 (br. *d*, *J* = 10.2), 4.32 (*m*)	3.55 (br. *d*, *J* = 10.8), 4.37 (*m*)	4.86[c])
Me(6‴)					1.65 (*d*, *J* = 6.4)
		Ara″	Ara″	Ara″	
H–C(1⁗)		4.82 (*d*, *J* = 7.8)	4.80 (*d*, *J* = 7.2)	4.83 (*d*, *J* = 7.3)	
H–C(2⁗)		4.47 (*dd*, *J* = 8.8, 7.8)	4.48 (*dd*, *J* = 8.8, 7.2)	4.45 (*dd*, *J* = 8.8, 7.3)	
H–C(3⁗)		4.11[c])	4.13[c])	4.16[c])	
H–C(4⁗)		4.23[c])	4.14[c])	4.30[c])	
CH_2(5⁗)		3.73 (br. *d*, *J* = 11.7), 4.30[c])	3.72 (br. *d*, *J* = 11.0), 4.32[c])	3.76 (br. *d*, *J* = 10.8), 4.30[c])	

[a]) Measured in C_5D_5N/D_2O. [b]) 600 MHz. [c]) Overlapping.

Scheffarboside C (**3**) was obtained as white amorphous powder. The positive-ion mode HR-ESI-MS of **3** displayed a $[M+Na]^+$ at m/z 1037.5305 ($C_{51}H_{82}NaO_{20}^+$). Acid hydrolysis of **3** afforded, in addition to hederagenin, the sugar components rhamnose and arabinose. Compound **3** was assigned the structure of 3-*O*-(*O*-α-arabinopyranosyl-(1 → 4)-*O*-α-arabinopyranosyl-(1 → 3)-*O*-α-rhamnopyranosyl-(1 → 2)-α-arabinopyranosyl)hederagenin[1]).

Analysis of the NMR data of compound **3** and comparison with those of **2** showed that they possessed the same saccharide chain at C(3) while the aglycone was the point of difference. The main difference in the ^{13}C-NMR was the presence of a CH_2 group at δ 63.8, indicating the presence of a CH_2OH function instead of a Me(23), as also supported by the upfield shifts of C(3) (δ 81.0), C(5) (δ 47.6), and C(24) (δ 14.1). The ^{1}H,^{1}H-COSY, HSQC, HMBC, and ROESY data, led to the assignment of all protons and C-atoms.

Scheffarboside D (**4**), a white amorphous powder, had the molecular formula $C_{69}H_{112}O_{33}$, as determined by HR-ESI-MS analysis (m/z 1491.6993, $[M+Na]^+$). The presence of an ester absorption at 1736 cm^{-1} was observed in the IR spectrum. On acid hydrolysis, compound **4** afforded oleanolic acid as aglycone and glucose, rhamnose, and arabinose as sugar components. On alkaline hydrolysis, compound **4** yielded compound **2**, identified by comparing with an authentic sample. Besides, compound **4** also provided glucose and rhamnose as C(28) ester sugar units. Compound **4** was assigned the structure of 3-*O*-(*O*-α-arabinopyranosyl-(1 → 4)-*O*-α-arabinopyranosyl-(1 → 3)-*O*-α-rhamnopyranosyl-(1 → 2)-α-arabinopyranosyl)oleanolic acid *O*-α-rhamnopyranosyl-(1 → 4)-*O*-β-glucopyranosyl-(1 → 6)-β-glucopyranosyl ester[1]).

The ^{13}C-NMR spectrum of **4** showed 69 signals, of which 30 were assigned to a triterpenoid moiety and 39 to the saccharide portion. The signals for C(3) at δ 88.5 and for C(28) at δ 176.4 established that **4** was a bidesmoside. Chemical shifts of H–C(1′) of Glc (δ 6.18) and C(1′) of Glc (δ 95.2) indicated that this sugar was involved in an ester linkage with the C(28) carboxylic group. The sugar units were defined by the HMBC experiments: key correlations were observed between H–C(1′) of Glc (δ 6.18) and C(28) (δ 176.4), H–C(1″) of Glc′ (δ 4.96) and C(6′) of Glc (δ 68.6), and H–C(1‴) of Rha (δ 5.75) and C(4″) of Glc″ (δ 78.0).

Comparison of the spectral data with the reported values allowed us to identify other compounds to be quinatoside A [7], hederagenin[1]) 3-(α-L-arabinopyranoside) [8], eleutheroside K [9], CP_3 [10], and sieboldianoside A [10].

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Experimental Part

General. Column chromatography (CC): silica gel (200–300 mesh; *Qingdao Marine Chemical*, China), *RP-18* silica gel (20–45 μ; *Fuji Silica Chemical,* Japan), polymer gel *DM-130* (*Shandong Lukang Pharmaceutical,* China), *MCI* gel *CHP20-P* (*Mitsubishi Chemical Co.* Japan), and *Sephadex LH-20* (*Pharmacia Fine Chemical Co. Ltd*). TLC: *GF 254* silica gel plates (*Yantai Marine Chemical Co. Ltd*, China); detection by spraying with 10% H_2SO_4 soln. followed by heating. ORD: *Perkin-Elmer 341* polari-

meter. IR: *Perkin-Elmer 577-IR* spectrometer; in cm^{-1}. NMR: *Bruker AM-400* and *AM-600* instrument; $SiMe_4$ as internal standard; δ in ppm, J in Hz. ESI-MS, MS/MS, and HR-ESI-MS: *Finnigan LCQ-DECA* instrument.

Plant Material. The stems of *Schefflera arboricola* were collected in June 2004 in Fujian province, China, and identified by Prof. *Shu-Rong Che*, Fujian College of Traditional Chinese Medicine. A voucher specimen (SA 040807) was deposited in our laboratory.

Extraction and Isolation. The fresh stems (12.5 kg) of *Schefflera arboricola* were extracted twice with hot 95% aq. EtOH to yield the extract. The extract was evaporated to yield a syrup, and the syrup was partitioned successively with petroleum ether/H_2O, AcOEt/H_2O, and BuOH/H_2O to afford a BuOH fraction. The BuOH fraction was subjected to CC (*DM-130* polymer gel, H_2O, 30% EtOH, 50% EtOH, 70% EtOH, 95% EtOH). The 70% EtOH fraction was resubjected to CC (silica gel, $CHCl_3$/MeOH/H_2O 85:15:0, 80:20:1, 75:25:1, 70:30:1, 70:30:5, 60:40:5): 9 fractions. Each fraction was further purified by CC (*MCI* gel, 30%, 50%, 70%, and 95% EtOH) and repeatedly resubjected to CC (*RP-C18*, 60–90% MeOH/H_2O and finally purified by CC (*Sephadex LH-20*, MeOH/H_2O 1:1): **1** (200 mg), **2** (250 mg), **3**, (150 mg), **4** (300 mg), and five known compounds.

Scheffarboside A (*= (3β)-3-[*(O-*β*-*Glucuronopyranosyl-(1 → 3)*-O-*α*-*6-deoxymannopyranosyl-(1 → 2)-α-arabinopyranosyl)oxy]-3-hydroxyolean-12-en-28-oic Acid*; **1**): White amorphous powder. $[\alpha]_D^{20} = -6.0$ ($c = 0.12$, pyridine/H_2O 3:1). IR (KBr): 3421, 2943, 1693, 1612, 1387, 1265, 1055, 642. ^{1}H-NMR: *Table 2*. ^{13}C-NMR: *Table 1*. ESI-MS (neg.): 909 ($[M-H]^-$). HR-ESI-MS (pos.): 933.4855 ($[M+Na]^+$, $C_{47}H_{74}NaO_{17}^+$; calc. 933.4824).

Scheffarboside B (*= (3β)-3-[(*O-*α*-*Arabinopyranosyl-(1 → 4)*-O-*α*-*arabinopyranosyl-(1 → 3)*-O-*α*-*6-deoxymannopyranosyl-(1 → 2)-α-arabinopyranosyl)oxy]-3-hydroxyolean-12-en-28-oic Acid*; **2**): White amorphous powder. $[\alpha]_D^{20} = -12.2$ ($c = 0.31$, pyridine). IR (KBr): 3419, 2941, 1693, 1647, 1456, 1387, 1257, 1059, 781. ^{1}H-NMR: *Table 2*. ^{13}C-NMR: *Table 1*. ESI-MS (neg.): 997 ($[M-H]^-$). HR-ESI-MS (pos.): 1021.5300 ($[M+Na]^+$, $C_{51}H_{82}NaO_{19}^+$, calc. 021.5348).

Scheffarboside C (*= (3β,4α)-3-(*O-*α*-*Arabinopyranosyl-(1 → 4)*-O-*α*-*arabinopyranosyl-(1 → 3)*-O-*α*-*6-deoxymannopyranosyl-(1 → 2)-α-arabinopyranosyl)oxy]-3,23-dihydroxyolean-12-en-28-oic Acid*; **3**): White amorphous powder. $[\alpha]_D^{20} = +1.5$ ($c = 0.32$, pyridine). IR (KBr): 3419, 2943, 1697, 1637, 1460, 1387, 1257, 1057, 781. ^{1}H-NMR: *Table 2*. ^{13}C-NMR: *Table 1*. ESI-MS (neg.): 1013 ($[M-H]^-$). HR-ESI-MS (pos.): 1037.5305 ($[M+Na]^+$, $C_{51}H_{82}NaO_{20}^+$, calc. 1037.5297).

Scheffarboside D (*= (3β)-3-[(*O-*α*-*Arabinopyranosyl-(1 → 4)*-O-*α*-*arabinopyranosyl-(1 → 3)*-O-*α*-*6-deoxymannopyranosyl-(1 → 2)-α-arabinopyranosyl)oxy]-3-hydroxyolean-12-en-28-oic Acid* O-*α*-*6-Deoxymannopyranosyl-(1 → 4)*-O-*β*-*glucopyranosyl-(1 → 6)-β-glucopyranosyl*) *Ester*; **4**): White amorphous powder. $[\alpha]_D^{20} = -27.8$ ($c = 0.35$, pyridine/H_2O 3:1). IR (KBr): 3415, 2941, 1736, 1647, 1458, 1388, 1259, 1061, 783. ^{1}H-NMR: *Table 2*. ^{13}C-NMR: *Table 1*. ESI-MS (pos.): 1491 ($[M+Na]^+$). HR-ESI-MS: 1491.6993 ($[M+Na]^+$, $C_{69}H_{112}NaO_{33}^+$; calc. 1491.6984).

Acid Hydrolysis. Each saponin (15 mg) was dissolved in 10% HCl soln. (10 ml) and heated at 100° for 1.5 h. The soln. was diluted with H_2O and extracted with AcOEt. Evaporation of the org. phase resulted in the aglycone. The aq. layer was evaporated and dried *in vacuo* to give the sugar moieties. The sugars were identified by co-TLC with authentic samples.

Basic Hydrolysis. A soln of saponin **4** (15 mg) in 0.5M KOH (25 ml) was refluxed for 1.5 h. The pH of the mixture was adjusted to 7 with 1M HCl, and the mixture was extracted with BuOH. The BuOH was evaporated to give **2**. The aq. layer was evaporated and dried *in vacuo* to give the sugar moieties. The sugar residue was dissolved in MeOH, and the sugars were identified by co-TLC with authentic samples.

Cytotoxicity in vitro. The human A549 lung epithelial cell line and the mouse P388 leukemia cell line assays were performed. The results showed that **2** indicated moderate activities at $1 \cdot 10^{-6}$ mol/l.

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