Unusual Nortriterpenoid Saponins from *Stauntonia chinensis*

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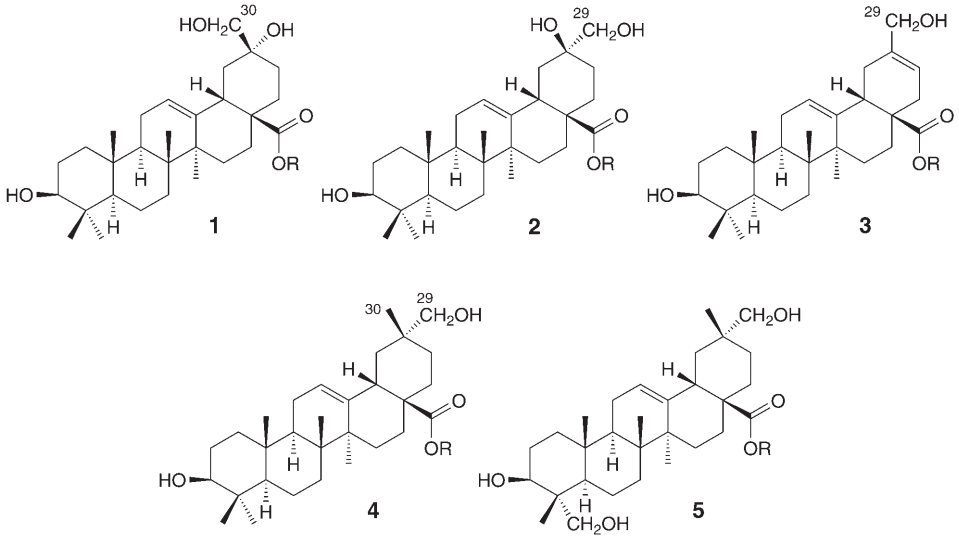
Four new saponins, yemuosides YM_{17}–YM_{20} (**1**–**4**, resp.), were isolated from the rattan of *Stauntonia chinensis* DC. (Lardizabalaceae) along with a known saponin, nipponoside D (**5**). Their structures were elucidated by spectroscopic analysis and chemical evidence as 20,30-dihydroxy-29-noroleanolic acid 28-*O*-*α*-L-rhamnopyranosyl-(1→4)-*β*-D-glucopyranosyl-(1→6)-*β*-D-glucopyranosyl ester (**1**), 20,29-dihydroxy-30-noroleanolic acid 28-*O*-*α*-L-rhamnopyranosyl-(1→4)-*β*-D-glucopyranosyl-(1→6)-*β*-D-glucopyranosyl ester (**2**), 29-hydroxy-30-norolean-20(21)-enolic acid 28-*O*-*α*-L-rhamnopyranosyl-(1→4)-*β*-D-glucopyranosyl-(1→6)-*β*-D-glucopyranosyl ester (**3**), 29-hydroxyoleanolic acid 28-*O*-*α*-L-rhamnopyranosyl-(1→4)-*β*-D-glucopyranosyl-(1→6)-*β*-D-glucopyranosyl ester (**4**), and 23,29-dihydroxyoleanolic acid 28-*O*-*α*-L-rhamnopyranosyl-(1→4)-*β*-D-glucopyranosyl-(1→6)-*β*-D-glucopyranosyl ester (**5**). Yemuoside YM_{17}–YM_{19} (**1**–**3**, resp.) contain novel unusual nortriterpene aglycones.

Introduction. – *Stauntonia chinensis* DC. has been used as a traditional Chinese medicine known as '*Ye Mu Gua*'. The evergreen herb grows in southern China and belongs to the family Lardizabalaceae. Plants of Lardizabalaceae are known to be rich in triterpenoid saponins [1]. Previous studies on *S. chinensis* afforded a series of noroleanane-type triterpenoid saponins [2–6]. In this paper, we report the isolation and structural elucidation of four new saponins, yemuosides YM_{17}–YM_{20} (**1**–**4**, resp.), along with a known saponin, nipponoside D (**5**) [7], from the rattan of *S. chinensis*. Yemuoside YM_{17}–YM_{19} (**1**–**3**, resp.) contain novel unusual nortriterpene aglycones.

Results and Discussion. –Yemuoside YM_{17} (**1**) was obtained as white amorphous powder, which gave positive results for the *Liebermann–Burchard* reaction and *Molisch* reagent. Its molecular formula was determined as $C_{47}H_{76}O_{19}$ according to the $[M+NH_4]^+$ peak at *m*/*z* 962.5323 (calc. for $C_{47}H_{80}NO_{19}^+$: 962.5325) in the positive-ion HR-ESI-Q-TOF-MS. After acid hydrolysis and derivatization of **1** by the method of *Hara et al.* [8], the GC analysis revealed the presence of L-rhamnose and D-glucose in an approximate ratio of 1:2. The IR spectrum of **1** showed an absorption band at 1733 cm^{-1}, indicating the presence of ester C=O group. In the ESI-IT-MS^n experiments, the MS^2 spectrum of the ion at *m*/*z* 967 ($[M+Na]^+$) gave a positive fragment at



R = α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl

m/*z* 493 ([470 + Na]$^+$), and the MS^2 spectrum of the ion at *m*/*z* 943 ([*M* − H]$^-$) gave negative fragments at *m*/*z* 473 ([*M* − H − 470]$^-$) and 469 ([470 − H]$^-$), confirming that the sugar chain of **1** consisted of two D-glucose residues and one L-rhamnose residue (470 = 162 + 162 + 146), and suggesting that the sugar chain was connected to **1** by an ester bond based on the fact that the cleavage readily occurs at the ester linkage of glycosides in CID experiments, and the charge resides either in the sugar moiety or in the aglycone moiety [9]. The MS^3 spectrum of the ion at *m*/*z* 493 ([470 + Na]$^+$) gave positive fragments at *m*/*z* 475, 447, 421, 405, 349, 347, 331, 289, and 203. This fragmentation pattern was in agreement with the pattern observed for rhamnopyranosyl-(1 → 4)-glucopyranosyl-(1 → 6)-glucopyranosyl [9]. The planar structure of the aglycone was determined based on the detailed analysis of the information from the COSY and HMBC experiments (*Fig. 1*). The relative configuration was established from the correlations in the NOESY experiment (*Fig. 2*). Thus, the aglycone of **1** was determinated as 20,30-dihydroxy-29-noroleanolic acid. The signals of the sugar moiety were assigned based on the COSY and TOCSY experiments. The HMBC correlation at δ(H) 6.22/δ(C) 176.3 indicated that the sugar chain was attached at C(28) through an ester bond. The HMBC correlations at δ(H) 4.95/δ(C) 69.4 and δ(H) 5.83/δ(C) 78.3 confirmed the interglucosidic linkages. The coupling constants and chemical shifts of the anomeric H-atom signals at δ 6.22 (*d*, *J* = 8.1, 1 H), 4.95 (*d*, *J* = 7.6, 1 H) and 5.83 (br. *s*, 1 H) rendered the anomeric configurations of the sugars to be α-rhamnose and β-glucose (see the *Table* in the *Exper. Part*). Therefore, **1** was determined as 20,30-dihydroxy-29-noroleanolic acid 28-*O*-α-L-rhamnopyranosyl-(1 → 4)-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranosyl ester, named yemuoside YM$_{17}$.

Yemuoside YM$_{18}$ (**2**) was obtained as white amorphous powder, which gave positive results for the *Liebermann–Burchard* reaction and *Molisch* reagent. Its molecular

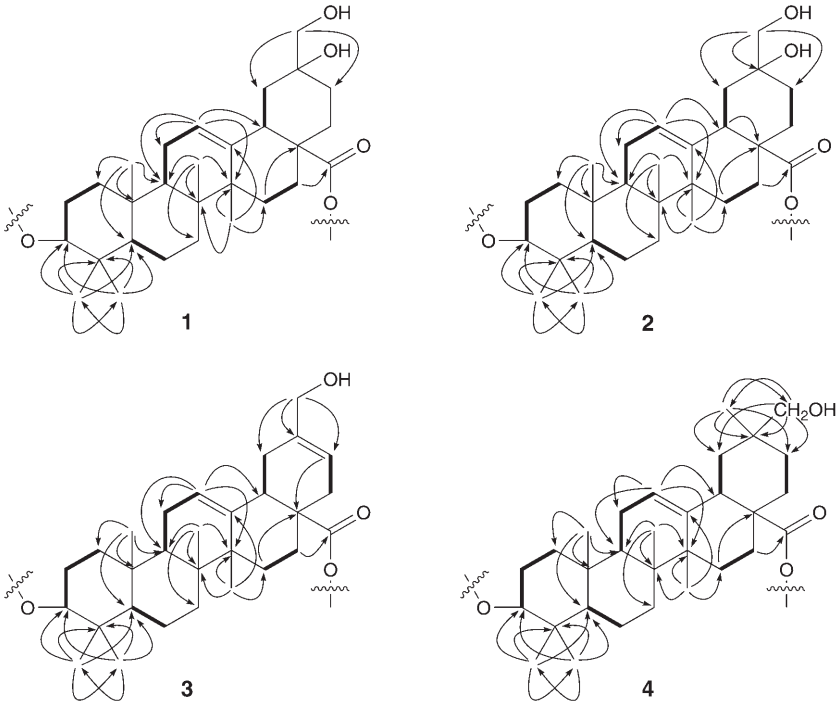


Fig. 1. *Key HMBC* (→) *and COSY* (**—**) *correlations of the aglycones of* **1**–**4**

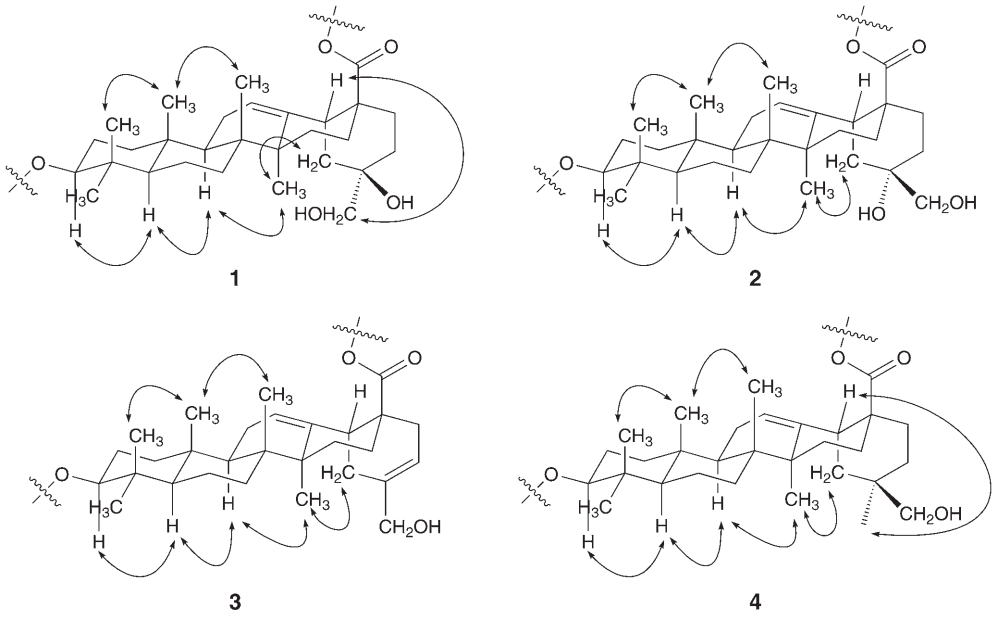


Fig. 2. *Key NOESY* (↔) *correlations of the aglycones of* **1**–**4**

formula was determined as $C_{47}H_{76}O_{19}$ according to the $[M+NH_4]^+$ peak at *m/z* 962.5348 (calc. for $C_{47}H_{80}NO_{19}^+$: 962.5325) in the positive HR-ESI-Q-TOF-MS. The ^{1}H- and ^{13}C-NMR data (see the *Table* in the *Exper. Part*) of the sugar chain of **2** were about the same as those of **1**, suggesting that **2** possessed the same sugar chain (rhamnopyranosyl-(1 → 4)-glucopyranosyl-(1 → 6)-glucopyranosyl). The IR spectrum, ESI-IT-MS^n experiments, and COSY, TOCSY, and HMBC experiments confirmed the above deduction. The COSY and HMBC experiments (*Fig. 1*) showed that the aglycone had the same planar structure as in **1**. Detailed comparison of the ^{1}H- and ^{13}C-NMR data of the aglycone moiety of **2** with those of **1** revealed differences in rings D and E (especially ring E). The NOESY experiment (*Fig. 2*) revealed the same relative configuration as **1**, except for the configuration of C(20). In the NOESY spectrum, the chemical shifts of H–C(18) and CH_2(29) were, however, too close to definitively exclude a correlation between these H-atoms in **2**. The equatorial orientation of CH_2(29) in **2** could be deduced by the comparison of the chemical shifts of CH_2(29) at δ(C) 72.1 in **2** and of CH_2(30) at δ(C) 65.8 in **1**, considering the γ-gauche effect. Thus, the aglycone of **2** was determined as 20,29-dihydroxy-30-noroleanolic acid, *i.e.*, the C(20)-epimer of the aglycone of **1**. The HMBC correlation at δ(H) 6.25/δ(C) 176.5 indicated that the sugar chain was attached at C(28) through as ester bond. Hence, **2** was determined as 20,29-dihydroxy-30-noroleanolic acid 28-*O*-α-L-rhamnopyranosyl-(1 → 4)-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranosyl ester, named yemuoside YM_{18}.

Yemuoside YM_{19} (**3**) was obtained as white amorphous powder, which gave positive results for the *Liebermann–Burchard* reaction and *Molisch* reagent. Its molecular formula was determined as $C_{47}H_{74}O_{18}$ according to the $[M+Na]^+$ peak at *m/z* 949.4787 (calc. for $C_{47}H_{74}NaO_{18}^+$: 949.4773) in the positive-ion HR-ESI-Q-TOF-MS. Compared with **1**, **3** possessed the same sugar chain as **1**, and the mass of aglycone of **3** was 456 u (18 u less than the mass of aglycone of **1**). Thus, **3** was considered to be derived from the dehydration of the aglycone moiety of **1**. Comparing the ^{13}C-NMR data (see the *Table* in the *Exper. Part*) of the aglycone of **3** with those of **1**, we found that the resonances of the oxygenated quaternary C-atom C(20) at δ(C) 72.1 and of an aliphatic CH_2 group in **1** disappeared, and that signals for an olefinic C-atom at δ(C) 117.1 and for an olefinic quaternary C-atom at δ(C) 137.9 due to an endocyclic C=C bond in **3** appeared, suggesting that **3** should be the dehydration derivative of **1** at C(20). The whole structure of the aglycone was determined, based on the detailed analysis of the information from the COSY, HMBC, and NOESY experiments (*Figs. 1* and *2*), as 29-hydroxy-30-norolean-20(21)-enolic acid. The HMBC correlation at δ(H) 6.22/δ(C) 176.0 indicated that the sugar chain was attached at C(28) through as ester bond. Hence, **3** was determined as 29-hydroxy-30-norolean-20(21)-enolic acid 28-*O*-α-L-rhamnopyranosyl-(1 → 4)-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranosyl ester, named yemuoside YM_{19}.

Yemuoside YM_{20} (**4**) was obtained as white amorphous powder, which gave positive results for the *Liebermann–Burchard* reaction and *Molisch* reagent. Its molecular formula was determined as $C_{48}H_{78}O_{18}$ according to the $[M+Na]^+$ peak at *m/z* 965.5090 (calc. for $C_{48}H_{78}NaO_{18}^+$: 965.5086) in the positive-ion HR-ESI-Q-TOF-MS. Compound **4** possessed the same sugar chain as **1**, and the mass of aglycone of **4** was 472 u. The structure of the aglycone was determined based on the detailed analysis of the COSY,

HMBC, and NOESY experiments (*Figs. 1* and *2*) to be 29-hydroxyoleanolic acid, also known as mesembryanthemoidigenic acid. The HMBC correlation at δ(H) 6.26/δ(C) 176.5 indicated that the sugar chain was attached at C(28) through as ester bond. This was confirmed by the glycosylation shift of $\Delta\delta$ −3.7 for C(28) compared to mesembryanthemoidigenic acid [10]. Accordingly, **4** was determined as 29-hydroxyoleanolic acid 28-*O*-α-L-rhamnopyranosyl-(1 → 4)-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranosyl ester, named yemuoside YM_{20}.

Plants of the family Lardizabalaceae are known to be rich in triterpenoid saponins [1]. Their aglycones are oleanolic acid, 30-noroleanolic acid, hederagenin, and 30-norhederagenin. Arjunolic acid and 30-norarjunolic acid are also found in a few species (*Akebia quinata* DECNE. [11] and *A. trifoliata* var. *australis* DIELS [12]). The aglycones mentioned above are derived from oleanolic acid through oxidation and/or demethylation. In general, the hydroxylation takes place at C(23) and/or C(2), and the demethylation occurs at C(20) to form the exocyclic C(20)=C(29) bond. In this paper, the reported yemuosides YM_{17} – YM_{19} (**1** – **3**, resp.) contain novel unusual nortriterpene aglycones, which were unknown before. For oleanane-type nortriterpenes, the demethylation occurring at C(20) to form an endocyclic C=C bond is rare, and the hydroxylation at both C(20) and C(29) was found for the first time.

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Experimental Part

General. Column chromatography (CC): silica gel (200–300 mesh; *Qingdao Haiyang Chemical Group Corporation*), *Sephadex LH-20* (*Amersham Biosciences AB*), and *ODS* (60–80 μm; *Merck*). TLC: silica gel GF_{254} (*Qingdao Haiyang Chemical Group Corporation*), and *RP-18* F_{254} (*Merck*). Prep. HPLC: *Shim-pack PRC-ODS* column (20 × 250 mm, 10 μm) at 10 ml/min with a *Shimadzu LC-8A* pump and a *Shimadzu RID-10A* refractive-index detector. GC: *HP-1701* column (0.25 mm × 30 m) with FID detector. Optical rotations: *JASCO P-1020* polarimeter. IR Spectra: *JASCO FT/IR-480 plus* spectrometer. NMR Spectra: *Bruker AVANCE 400* NMR spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C); in (D_5)pyridine. ESI-IT-MS: *Bruker Esquire 2000* mass spectrometer; HR-ESI-Q-TOF-MS: *Micromass* Q-TOF mass spectrometer; in *m*/*z*.

Plant Material. *S. chinensis* DC. was collected in Jiangxi Province in November 2004 by *LifeTech Pharmaceuticals Ltd.*, Guangzhou, and identified by Traditional Chinese Medicine Department, Shenzhen Institute of Drug Control. A voucher specimen is deposited with the Research Center of Traditional Chinese Medicine and Natural Products, Shenzhen, China.

Extraction and Isolation. The air-dried rattan of *S. chinensis* (20 kg) was chopped and refluxed with 60% EtOH (200 l) for two times (2 h per each time). After evaporation of EtOH *in vacuo*, the aq. residue was extracted with BuOH (20 l) for three times. A portion (150 g) of the BuOH extract was subjected to CC (silica gel; $CHCl_3$/MeOH/H_2O 100:0:0, 98:2:0, 95:5:0, 90:10:0, 80:20:2, 70:30:5, 60:40:8, 0:100:0) to yield eight *Fractions*. *Fr. 6* ($CHCl_3$/MeOH/H_2O 70:30:5) was further applied to *ODS* CC (MeOH/H_2O 0:100, 10:90, 30:70, 50:50, 70:30, 90:10, 100:0) to give seven subfractions. *Subfr. 4* (MeOH/H_2O 50:50) was purified on a *Sephadex LH-20* column with MeOH/H_2O 1:1. Then, repeated prep. HPLC with MeOH/H_2O 55:45 gave **1** (28.3 mg; t_R 21.4 min), **2** (12.9 mg; t_R 31.5 min), **3** (8.6 mg; t_R 56.6 min), **4** (19.2 mg; t_R 52.1 min), **5** (13.1 mg; t_R 14.6 min).

Table. *NMR Spectroscopic Data for* **1**–**4**. At 400 (^{1}H) and 100 MHz (^{13}C), in (D_5)pyridine; δ in ppm, J in Hz.

	1		**2**		**3**		**4**	
	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)
CH_2(1)	38.9	0.90–0.98 (*m*), 1.46–1.54 (*m*)	38.9	0.93–1.01 (*m*), 1.47–1.55 (*m*)	38.9	0.95–1.03 (*m*), 1.50–1.58 (*m*)	38.9	0.93–1.01 (*m*), 1.50–1.58 (*m*)
CH_2(2)	28.0	1.75–1.83 (*m*)	28.0	1.76–1.84 (*m*)	28.0	1.77–1.85 (*m*)	28.1	1.76–1.84 (*m*)
H–C(3)	78.1	3.42 (*dd*, *J* = 10.2, 5.8)	78.0	3.41 (*dd*, *J* = 10.2, 5.8)	78.0	3.42 (*dd*, *J* = 10.2, 5.8)	78.0	3.41 (*dd*, *J* = 10.2, 5.5)
C(4)	39.3		39.3		39.3		39.3	
H–C(5)	55.8	0.81 (*d*, *J* = 10.9)	55.8	0.84 (*d*, *J* = 10.9)	55.7	0.83 (*d*, *J* = 10.9)	55.8	0.83 (*d*, *J* = 11.3)
CH_2(6)	18.8	1.31–1.39 (*m*), 1.47–1.55 (*m*)	18.8	1.34–1.42 (*m*), 1.48–1.56 (*m*)	18.8	1.34–1.42 (*m*), 1.47–1.55 (*m*)	18.8	1.32–1.40 (*m*), 1.47–1.55 (*m*)
CH_2(7)	33.1	1.29–1.37 (*m*), 1.41–1.49 (*m*)	33.1	1.34–1.42 (*m*), 1.46–1.54 (*m*)	32.8	1.29–1.37 (*m*), 1.41–1.49 (*m*)	33.1	1.31–1.39 (*m*), 1.42–1.50 (*m*)
C(8)	39.9		39.9		40.0		39.9	
H–C(9)	48.0	1.57–1.65 (*m*)	48.1	1.61–1.69 (*m*)	48.1	1.62–1.70 (*m*)	48.1	1.61–1.69 (*m*)
C(10)	37.3		37.3		37.3		37.3	
CH_2(11)	23.7	1.81–1.89 (*m*)	23.7	1.83–1.91 (*m*)	23.7	1.87–1.95 (*m*)	23.8	1.88–1.96 (*m*)
H–C(12)	123.2	5.45 (*t*, *J* = 3.8)	122.5	5.47 (*t*, *J* = 3.8)	123.1	5.46 (*t*, *J* = 3.8)	122.8	5.46 (*t*, *J* = 3.8)
C(13)	143.4		144.4		143.6		144.3	
C(14)	42.1		42.1		41.9		42.1	
CH_2(15)	28.3	1.13–1.21 (*m*), 2.26–2.34 (*m*)	28.4	1.17–1.25 (*m*), 2.40 (br. *t*, *J* = 13.3)	28.6	1.07–1.15 (*m*), 2.31–2.39 (*m*)	28.3	1.11–1.19 (*m*), 2.34 (br. *t*, *J* = 13.7)
CH_2(16)	23.8	2.01–2.09 (*m*), 2.26–2.34 (*m*)	23.2	2.04–2.12 (*m*), 2.18–2.26 (*m*)	25.9	1.91–1.99 (*m*), 1.99–2.07 (*m*)	23.4	1.93–2.01 (*m*), 2.14–2.22 (*m*)
C(17)	47.0		47.3		45.6		47.3	
H–C(18)	43.4	3.30 (*dd*, *J* = 14.3, 4.4)	40.6	3.80–3.88 (*m*)	41.9	3.22 (*dd*, *J* = 10.6, 7.5)	41.1	3.30 (*dd*, *J* = 14.0, 4.4)
CH_2(19)	42.4	2.18–2.26 (*m*), 2.28–2.36 (*m*)	41.1	1.96–2.04 (*m*), 2.28 (*t*, *J* = 14.0)	32.5	2.27–2.35 (*m*), 2.52–2.60 (*m*)	40.9	1.40–1.48 (*m*), 2.09–2.17 (*m*)
C(20)	72.1		71.3		137.9		36.3	
CH_2(21)	30.7	1.89–1.97 (*m*), 2.06–2.14 (*m*)	29.2	1.82–1.90 (*m*)			28.8	1.24–1.32 (*m*), 1.70–1.78 (*m*)
H–C(21)					117.1	5.75 (br. *s*)		
CH_2(22)	33.8	1.94–2.02 (*m*)	31.4	1.93–2.01 (*m*), 2.60 (*td*, *J* = 13.3, 4.8)	36.5	2.30–2.38 (*m*), 2.60–2.68 (*m*)	32.0	1.83–1.91 (*m*), 1.93–2.01 (*m*)

Table (cont.)

	1		**2**		**3**		**4**	
	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)
Me(23)	28.7	1.21 (*s*)	28.7	1.21 (*s*)	28.7	1.21 (*s*)	28.7	1.20 (*s*)
Me(24)	16.5	1.01 (*s*)	16.5	1.02 (*s*)	16.4	1.03 (*s*)	16.5	1.02 (*s*)
Me(25)	15.6	0.90 (*s*)	15.6	0.92 (*s*)	15.6	0.94 (*s*)	15.6	0.93 (*s*)
Me(26)	17.5	1.09 (*s*)	17.5	1.15 (*s*)	17.4	1.13 (*s*)	17.5	1.14 (*s*)
Me(27)	25.9	1.23 (*s*)	26.0	1.26 (*s*)	26.9	1.26 (*s*)	26.0	1.24 (*s*)
C(28)	176.3		176.5		176.0		176.5	
CH_2(29)			72.1	3.86 (*s*)	66.1	4.29 (*s*)	73.6	3.53 (*s*)
CH_2(30)	65.8	4.03 (*s*)						
Me(30)							19.7	1.08 (*s*)
Sugar chain								
28-*O*-*Glc*								
H–C(1)	95.7	6.22 (*d*, *J* = 8.1)	95.7	6.25 (*d*, *J* = 8.1)	95.6	6.22 (*d*, *J* = 8.1)	95.6	6.26 (*d*, *J* = 8.1)
H–C(2)	73.8	4.07–4.15 (*m*)	73.8	4.09–4.17 (*m*)	73.7	4.10–4.18 (*m*)	73.8	4.09–4.17 (*m*)
H–C(3)	78.7	4.16–4.24 (*m*)	78.7	4.17–4.25 (*m*)	78.7	4.16–4.24 (*m*)	78.7	4.17–4.25 (*m*)
H–C(4)	70.8	4.25–4.33 (*m*)	70.7	4.34–4.42 (*m*)	70.9	4.23–4.31 (*m*)	70.8	4.28–4.36 (*m*)
H–C(5)	77.9	4.03–4.11 (*m*)	77.8	4.01–4.09 (*m*)	78.0	4.06–4.14 (*m*)	77.9	4.05–4.13 (*m*)
CH_2(6)	69.4	4.27–4.35 (*m*), 4.61–4.69 (*m*)	69.4	4.27–4.35 (*m*), 4.62 (*dd*, *J* = 11.9, 2.1)	69.3	4.28–4.36 (*m*), 4.62–4.70 (*m*)	69.2	4.29–4.37 (*m*), 4.63–4.71 (*m*)
28-*O*-Glc-6-*Glc*								
H–C(1)	105.0	4.95 (*d*, *J* = 7.6)	105.2	4.93 (*d*, *J* = 7.4)	104.9	5.00 (*d*, *J* = 7.9)	104.9	4.97 (*d*, *J* = 7.9)
H–C(2)	75.2	3.93 (*t*, *J* = 8.2)	75.2	3.93 (*t*, *J* = 8.5)	75.2	3.94 (*t*, *J* = 8.5)	75.3	3.93 (*t*, *J* = 8.2)
H–C(3)	76.4	4.09–4.17 (*m*)	76.4	4.10–4.18 (*m*)	76.5	4.12–4.20 (*m*)	76.5	4.10–4.18 (*m*)
H–C(4)	78.3	4.38 (*t*, *J* = 9.2)	78.3	4.40 (*t*, *J* = 9.2)	78.3	4.41 (*t*, *J* = 9.2)	78.2	4.41 (*t*, *J* = 9.2)
H–C(5)	77.2	3.66 (br. *d*, *J* = 9.2)	77.1	3.65 (br. *d*, *J* = 9.2)	77.1	3.68 (br. *d*, *J* = 9.2)	77.1	3.65 (br. *d*, *J* = 9.6)
CH_2(6)	61.3	4.05–4.13 (*m*), 4.15–4.23 (*m*)	61.3	4.05–4.13 (*m*), 4.17–4.25 (*m*)	61.3	4.06–4.14 (*m*), 4.17–4.25 (*m*)	61.2	4.04–4.12 (*m*), 4.15–4.23 (*m*)
28-*O*-Glc-6-Glc-4-*Rha*								
H–C(1)	102.7	5.83 (br. *s*)	102.7	5.84 (br. *s*)	102.7	5.84 (br. *s*)	102.7	5.84 (br. *s*)
H–C(2)	72.5	4.63–4.71 (*m*)	72.5	4.67 (br. *s*)	72.5	4.62–4.70 (*m*)	72.5	4.62–4.70 (*m*)
H–C(3)	72.7	4.55 (*dd*, *J* = 9.2, 3.4)	72.7	4.55 (*dd*, *J* = 9.2, 3.1)	72.7	4.54 (*dd*, *J* = 9.2, 3.1)	72.7	4.54 (*dd*, *J* = 9.2, 3.1)
H–C(4)	73.9	4.27–4.35 (*m*)	73.9	4.28–4.36 (*m*)	73.9	4.27–4.35 (*m*)	73.9	4.27–4.35 (*m*)
H–C(5)	70.3	4.89–4.97 (*m*)	70.3	4.90–4.98 (*m*)	70.3	4.90–4.98 (*m*)	70.2	4.91–4.99 (*m*)
Me(6)	18.5	1.68 (*d*, *J* = 6.2)	18.5	1.68 (*d*, *J* = 6.2)	18.4	1.69 (*d*, *J* = 6.2)	18.5	1.69 (*d*, *J* = 6.2)

*20,30-Dihydroxy-29-noroleanolic Acid 28-*O*-α-*L*-Rhamnopyranosyl-(1 → 4)-β-*D*-glucopyranosyl-(1 → 6)-β-*D*-glucopyranosyl Ester* (**1**). White amorphous powder. $[\alpha]_D^{26} = -22.5$ ($c = 0.10$, MeOH/H_2O 3:1). IR (KBr): 3405, 2936, 1733, 1636, 1448, 1387, 1065. ^{1}H- and ^{13}C-NMR: see the *Table*. ESI-IT-MS (pos.): 967 ($[M+Na]^+$). ESI-IT-MS^2 (pos.; 967): 493 ($[470+Na]^+$). ESI-IT-MS^3 (pos.; 967 – 493): 475, 447, 421, 405, 349, 347, 331, 289, 203. ESI-IT-MS (neg.): 943 ($[M-H]^-$). ESI-IT-MS^2 (neg.; 943): 473 ($[M-H-470]^-$), 469 ($[470-H]^-$). HR-ESI-Q-TOF-MS (pos.): 962.5323 ($[M+NH_4]^+$, $C_{47}H_{80}NO_{19}^+$; calc. 962.5325).

*20,29-Dihydroxy-30-noroleanolic Acid 28-*O*-α-*L*-Rhamnopyranosyl-(1 → 4)-β-*D*-glucopyranosyl-(1 → 6)-β-*D*-glucopyranosyl Ester* (**2**). White amorphous powder. $[\alpha]_D^{25} = +8.8$ ($c = 0.10$, MeOH). IR (KBr): 3405, 2937, 1745, 1635, 1446, 1385, 1065. ^{1}H- and ^{13}C-NMR: see the *Table*. ESI-IT-MS (pos.): 967 ($[M+Na]^+$). ESI-IT-MS^2 (pos.; 967): 493 ($[470+Na]^+$). ESI-IT-MS^3 (pos.; 967 – 493): 475, 447, 421, 405, 349, 347, 331, 289, 203. ESI-IT-MS (neg.): 943 ($[M-H]^-$). ESI-IT-MS^2 (neg.; 943): 473 ($[M-H-470]^-$), 469 ($[470-H]^-$). HR-ESI-Q-TOF-MS (pos.): 962.5348 ($[M+NH_4]^+$, $C_{47}H_{80}NO_{19}^+$; calc. 962.5325).

*29-Hydroxy-30-norolean-20(21)-enolic Acid 28-*O*-α-*L*-Rhamnopyranosyl-(1 → 4)-β-*D*-glucopyranosyl-(1 → 6)-β-*D*-glucopyranosyl Ester* (**3**). White amorphous powder. $[\alpha]_D^{26} = -10.9$ ($c = 0.07$, MeOH). IR (KBr): 3424, 2938, 1732, 1635, 1446, 1386, 1066. ^{1}H- and ^{13}C-NMR: see the *Table*. ESI-IT-MS (pos.): 949 ($[M+Na]^+$). ESI-IT-MS^2 (pos.; 949): 493 ($[470+Na]^+$). ESI-IT-MS^3 (pos.; 949 – 493): 475, 447, 421, 405, 349, 347, 331, 289, 203. ESI-IT-MS (neg.): 925 ($[M-H]^-$). ESI-IT-MS^2 (neg.; 925): 455 ($[M-H-470]^-$), 469 ($[470-H]^-$). HR-ESI-Q-TOF-MS (pos.): 949.4787 ($[M+Na]^+$, $C_{47}H_{74}NaO_{18}^+$; calc. 949.4773).

*29-Hydroxyoleanolic Acid 28-*O*-α-*L*-Rhamnopyranosyl-(1 → 4)-β-*D*-glucopyranosyl-(1 → 6)-β-*D*-glucopyranosyl Ester* (**4**). White amorphous powder. $[\alpha]_D^{26} = -3.3$ ($c = 0.11$, MeOH). IR (KBr): 3404, 2935, 1747, 1636, 1461, 1385, 1062. ^{1}H- and ^{13}C-NMR: see the *Table*. ESI-IT-MS (pos.): 965 ($[M+Na]^+$). ESI-IT-MS^2 (pos.; 965): 493 ($[470+Na]^+$). ESI-IT-MS^3 (pos.; 965 – 493): 475, 447, 421, 405, 349, 347, 331, 289, 203. ESI-IT-MS (neg.): 941 ($[M-H]^-$). ESI-IT-MS^2 (neg.; 941): 471 ($[M-H-470]^-$), 469 ($[470-H]^-$). HR-ESI-Q-TOF-MS (pos.): 965.5090 ($[M+Na]^+$, $C_{48}H_{78}NaO_{18}^+$; calc. 965.5086).

Acid Hydrolysis and Derivatization of **1**, *and GC Analysis.* Compound **1** (2 mg) was heated in an ampule with 5 ml of aq. 12% HCl at 90° for 2 h. The aglycone was extracted with $CHCl_3$, and the aq. residue was evaporated under reduced pressure. Then, 1 ml of dry pyridine and 2 mg of L-cysteine methyl ester hydrochloride (*Sigma*, USA) were added to the dry residue, and the mixture was heated at 60° for 2 h. The mixture was concentrated to dryness with N_2 gas, and to the residue was added 1-(trimethylsilyl)-1*H*-imidazole (*Fluka*, USA), followed by heating at 60° for 1 h. The resulting soln. was extracted with cyclohexane and H_2O, and the combined org. phase was submitted to GC analysis, performed by FID detector with N_2 as carrier gas. The injector temp. was set at 250°, and the column temp. program was as follows: the initial temp. of 200° was held constant for 5 min and then increased by 5°/min to the final temp. of 250°. The detector temp. was set at 280°. The standard monosaccharides (D-glucose and L-rhamnose; *Sigma*, USA) were subjected to the same reaction and GC analysis under the same conditions.

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