A Pair of New Nortriterpene Saponin Epimers from the Roots of *Gypsophila oldhamiana*

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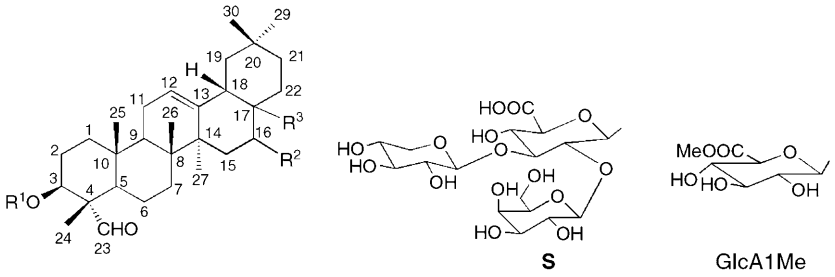
A pair of new oleanane-type nortriterpene saponin epimers, neogypsoside A (**1**) and B (**2**) (*Fig. 1*) with neogypsogenin A (**3**) and neogypsogenin B (**4**) as the two new aglycons, as well as the two known triterpene saponins **5** and **6** (*Fig. 1*), were isolated from the roots of *Gypsophila oldhamiana*. Their structures were determined by analysis of their NMR data. A possible biogenetic pathway to the nortriterpene saponins **1** and **2** is proposed (*Scheme 2*).

1. Introduction. – *Gypsophila oldhamiana* (MIQ.) (Caryophyllaceae) is widely distributed in the north regions of China and has been used as an alternative remedy to the most common traditional Chinese medicine Yin-Chai-Hu (roots of *Stellria dichotoma* var. Lanceolata Bge), for the treatment of fever, consumptive disease, and infantile malnutrition syndrome [1]. Early chemical investigation of the roots of this species led to the isolation of saponins, sterols, and fatty acid [2–6]. During our efforts toward searching for saponins, we investigated the BuOH-soluble fraction of 70% EtOH/H_2O extracts from the roots of *G. oldhamiana.* As a result, a pair of new epimeric nortriterpene saponins, neogypsoside A (**1**) and B (**2**), based on two new aglycons, named neogypsogenin A (**3**) and neogypsogenin B (**4**), along with two known saponins, **5** and **6**, were isolated (*Fig. 1*). These latter were identified as 3-*O*-[*O*-β-D-galactopyranosyl-(1 $\rightarrow$ 2)-[*O*-β-D-xylopyranosyl-(1 $\rightarrow$ 3)]-β-D-glucopyranuronosyl] quillaic acid methyl ester (**5**), 3-*O*-[*O*-β-D-galactopyranosyl-(1 $\rightarrow$ 2)-[*O*-β-D-xylopyranosyl-(1 $\rightarrow$ 3)]-β-D-glucopyranuronosyl]gypsogenin methyl ester (**6**), respectively [3]. This report describes the structural elucidation and possible biogenetic implication of two new nortriterpene saponins **1** and **2**.

2. Results and Discussion. – Neogypsoside A (**1**) was obtained as an optically active white amorphous powder. Its IR spectrum revealed the presence of OH groups at 3439 cm^{-1}, carboxyl groups at 1709 cm^{-1}, a C=C bond at 1628 cm^{-1}, and C–O–C bonds at 1041 cm^{-1}. The HR-ESI-MS showed an ion peak at *m*/*z* 933.4480 ($[M+Na]^+$), which suggested the molecular formula $C_{46}H_{70}O_{18}$. The structure of the aglycon of **1** was determined by the NMR data (^{1}H- and ^{13}C-NMR, HSQC, HMBC; see *Table 1*) and comparison with those of melandrigenin [7] to be (3β,17α)-3-hydroxy-28-norolean-12-ene-16,23-dione, a new 28-nortriterpene aglycon named neogypsogenin A (**3**) with (17α)-configuration and thus a *trans* D/E ring junction. Acid hydrolysis of **1** by 2% H_2SO_4



1 R^1 = **S**, R^2 = =O, R^3 = α-H
2 R^1 = **S**, R^2 = =O, R^3 = β-H
3 R^1 = H, R^2 = =O, R^3 = α-H
4 R^1 = H, R^2 = =O, R^3 = β-H
5 R^1 = **S**, R^2 = α-H, R^3 = β-COOMe
6 R^1 = **S**, R^2 = H, R^3 = β-COOMe
7 R^1 = GlcA1Me, R^2 = =O R^3 = α-H

Fig. 1. *The structures of compounds* **1**–**7**

in H_2O/MeOH 1:1 gave (neogypsogenin-A-3-yl) glucopyranosiduronic acid methyl ester (**7**), xylose, and galactose. Further acid hydrolysis of **7** by 5% H_2SO_4 in dioxane/H_2O 1:1 gave neogypsogenin A (**3**) and glucuronic acid. The sugars were identified as D-xylose, D-galacose, and D-glucuronic acid by their optical rotations and TLC comparison with authentic samples. The NMR data of **1** (^{1}H- and ^{13}C-NMR, HSQC, HMBC (*Table 2*), and ROESY) established the connectivities of the sugar moieties. Therefore, the structure of compound **1** was determined as neogypsogenin A 3-*O*-[*O*-β-D-galactopyranosyl-(1 → 2)-[*O*-β-D-xylopyranosyl-(1 → 3)]-β-D-glucopyranosiduronic acid.

The ^{1}H- and ^{13}C-NMR, HSQC, and HMBC data of **1** showed the presence of six angular Me groups (δ(H) 1.46, 0.78, 0.71, 1.01, 0.93, and 0.83, correlated to δ(C) 10.3, 15.0, 16.2, 24.9, 32.7, and 24.1 in the HSQC plot, resp.), a ketone carbonyl atom at δ 212.9, an aldehydic C-atom at δ 209.4, and a trisubstituted C=C bond at δ 117.0 and 142.1, which were compatible with an oleanane-type 28-nortriterpene aglycon with (17α)-configuration, *i.e.*, a *trans* D/E ring junction [7][8]. The assignments of the NMR data of the aglycon moiety were readily recognized on the basis of the HSQC and HMBC (see *Table 1*) experiments, in accordance with those of melandrigenin [7], except for those of C(20), C(21), and C(22). The chemical shift changes of C(20), C(21), and C(22) were due to the OH group having been removed from C(21). A ROESY experiment showed that H–C(17) and Me(27) as well as H–C(18) and Me(30) were correlated, but no correlation between H–C(17) and H–C(18) was found (*Fig. 2*), indicating that H–C(17) and H–C(18) were not on the same side of the molecular skeleton. Since H–C(17) pointed to the α-side, and H–C(18) to the β-side, the *trans* D/E ring junction of the aglycon was further confirmed. The remaining part of the NMR data of **1**, attributed to the fragment $C_{17}H_{26}O_{15}$, arose from the saccharide moiety. The ^{1}H- and ^{13}C-NMR, HSQC, and HMBC data (*Table 2*) showed that **1** contained three anomeric C-atoms at δ 103.4, 103.7, and 104.5, which correlated with the protons at δ 4.90 (*d*, *J* = 7.5 Hz), 5.53 (*d*, *J* = 7.7 Hz), and 5.30 (*d*, *J* = 7.7 Hz) in the HSQC plot, indicating the presence of three sugar units in the β-D-anomeric form. The positions of connectivity of the sugars were determined by comparing the spectral data with those reported [3] and were confirmed by HSQC, HMBC, and ROESY experiments. The galactose and xylose units were found to be terminal and bound to C(2) and C(3) of the glucuronic acid unit, respectively.

Neogypsoside B (**2**), an optically active white powder, had the same molecular formula $C_{46}H_{70}O_{18}$ as **1** according to the ion peak at *m*/*z* 933.4448 ([*M* + Na]$^+$) in the HR-ESI-MS. The IR spectrum showed absorptions at 3429 (OH), 1707 (C=O), and 1632

Table 1. *NMR Data for Aglycon Moieties of* **1** *and* **2** *in* C_5D_5N. δ in ppm, J in Hz.

	1			**2**		
	HSQC		HMBC	HSQC		HMBC
	δ(C)	δ(H)		δ(C)	δ(H)	
CH_2(1)	38.0	1.34–1.38 (*m*); 1.09–1.12 (*m*)	C(2)	37.3	1.35–1.39 (*m*); 0.80–0.82 (*m*)	
CH_2(2)	24.6	2.08–2.11 (*m*); 1.82–1.87 (*m*)		24.6	2.09–2.13 (*m*); 1.82–1.85 (*m*)	
H–C(3)	83.0	4.03–4.06 (*m*)	C(24), C(23)	83.4	4.01–4.03 (*m*)	C(4), C(23), C(24)
C(4)	54.4	–		54.4	–	
H–C(5)	48.2	1.34–1.38 (*m*)	C(24), C(25), C(6), C(10)	47.9	1.34–1.36 (*m*)	C(4), C(6), C(10), C(24), C(25)
CH_2(6)	19.9	1.34–1.36 (*m*); 0.96–0.98 (*m*)		19.7	1.34–1.37 (*m*); 0.93–0.98 (*m*)	C(7); C(8)
CH_2(7)	32.0	1.35–1.37 (*m*); 1.05 (br. *s*)		31.7	1.32–1.33 (*m*); 0.96–1.10 (*m*)	C(5), C(9), C(26)
C(8)	38.4	–		39.3	–	
H–C(9)	46.7	1.67 (*t*, *J* = 7.0, 8.0)	C(10), C(5), C(25), C(8)	46.2	1.54 (*t*, *J* = 9.5, 8.5)	C(8), C(10), C(25), C(26)
C(10)	35.8	–		35.6	–	
CH_2(11)	23.3	2.28–2.32 (*m*); 1.82–1.87 (*m*)	C(10)	22.9	1.82–1.85 (*m*)	
H–C12)	117.0	5.38 (br. *s*)		122.1	5.33 (br. *s*)	C(9), C(11), C(18)
C(13)	142.1	–		142.1	–	
C(14)	42.3	–		47.0	–	
CH_2(15)	43.5	2.59 (*d*, *J* = 15.4); 2.10 (*d*, *J* = 15.4)	C(27), C(14), C(17); C(13), C(16)	46.3	2.50 (*d*, *J* = 14.8); 1.93 (*d*, *J* = 14.8)	C(8), C(27), C(14); C(13), C(16), C(27) C(14)
H–C(16)	212.9	–		212.0	–	
H–C17)	49.1	1.91 (*td*, *J* = 12.0, 3.6)	C(22), C(16)	46.4	2.48 (*ddd*, *J* = 13.5, 5.8, 3.9)	C(16), C(18), C(21), C(22)
H–C(18)	36.4	2.28–2.32 (*m*)	C(20)	44.2	2.79 (br.)	C(17), C(19)
CH_2(19)	42.3	1.84–1.87 (*m*); 0.95 (*t*, *J* = 12.0)	C(30)	46.1	1.40–1.43 (*m*); 1.18–1.19 (*m*)	C(20), C(21), C(30); C(18)
C(20)	30.0	–		30.4	–	
CH_2(21)	37.1	1.32–1.33 (*m*); 0.77–0.79 (*m*)	C(17)	34.1	1.59 (*dd*, *J* = 13.5, 3.9); 1.11 (br. *d*, *J* = 13.3)	C(19), C(20), C(22), C(30)
CH_2(22)	22.8	1.34–1.37 (*m*); 1.95–1.99 (*m*)		20.7	2.14 (br. *d*, *J* = 14.3); 1.34–1.38 (*m*)	C(21)
H–C(23)	209.4	9.95 (*s*)	C(24), C(4)	209.0	9.95 (*s*)	C(4), C(24)
Me(24)	10.3	1.46 (*s*)	C(5), C(4), C(3)	10.5	1.47 (*s*)	C(3), C(4), C(5)
Me(25)	15.0	0.78 (*s*)	C(10)	14.9	0.79 (*s*)	C(5), C(9), C(10)
Me(26)	16.2	0.71 (*s*)	C(8), C(14)	17.0	0.83 (*s*)	C(8), C(9)
Me(27)	24.9	1.01 (*s*)	C(8), C(14), C(13)	26.4	1.16 (*s*)	C(8), C(13), C(15), C(16)
Me(29)	32.7	0.93 (*s*)	C(20), C(30), C(19)	32.8	0.81 (*s*)	C(19), C(20), C(21), C(30)
Me(30)	24.1	0.83 (*s*)	C(20)	22.9	0.85 (*s*)	C(19), C(20), C(21), C(29)

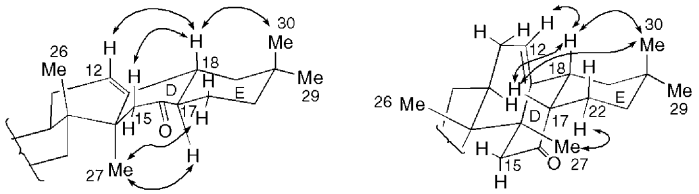
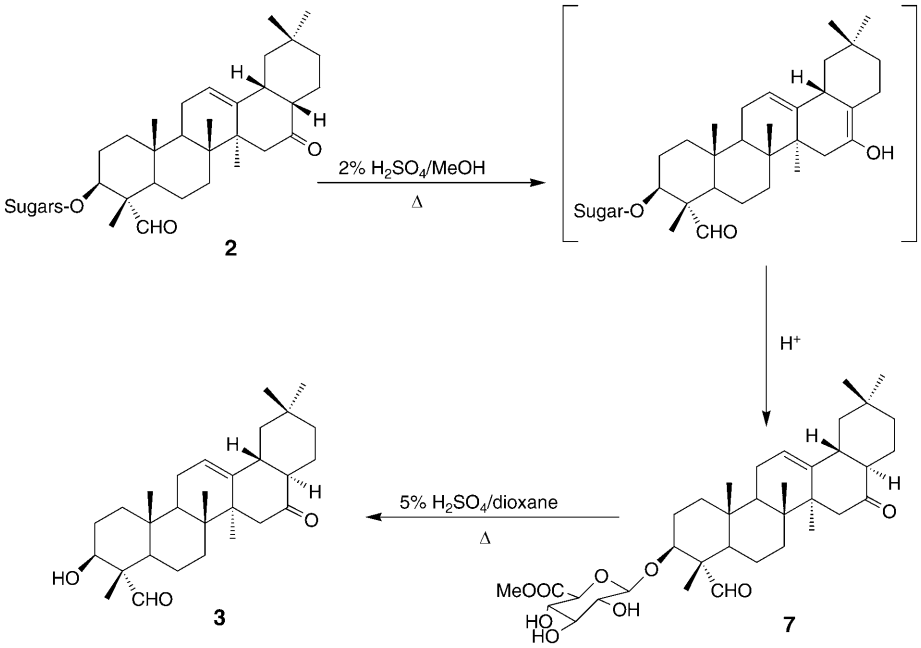


Fig. 2. *Selected ROESY correlations within Rings D and E for* **1** *and* **2**

Table 2. *NMR Data for Sugar Moieties of* **1** *and* **2** *in C_5D_5N.* δ in ppm, J in Hz.

	1			**2**		
	HSQC		HMBC	HSQC		HMBC
	δ(C)	δ(H)		δ(C)	δ(H)	
GlcA						
H–C(1)	103.4	4.90 (*d*, *J* = 7.5)	C(3) (agl.)	103.3	4.88 (*d*, *J* = 7.5)	C(3) (agl.), C(3) and C(4) (GlcA)
H–C(2)	78.1	4.34 (*dd*, *J* = 7.5, 8.9)	C(3) and C(1) (GlcA)	78.1	4.34 (*dd*, *J* = 7.5, 8.9)	C(3) and C(1) (GlcA)
H–C(3)	85.5	4.24 (*t*, *J* = 8.9)	C(4) and C(2) (GlcA), C(1) (Xyl)	85.6	4.24 (*t*, *J* = 8.9)	C(4) and C(2) (GlcA), C(1) (Xyl)
H–C(4)	70.7	4.43 (*t*, *J* = 8.9)	C(5) (GlcA)	70.7	4.43 (*t*, *J* = 8.9)	C(5) (GlcA)
H–C(5)	76.7	4.49 (*d*, *J* = 8.9)	C(4) and C(6) (GlcA)	76.7	4.50 (*d*, *J* = 8.9)	C(4) and C(6) (GlcA)
C(6)	171.1			171.1		
Xyl						
H–C(1)	104.5	5.30 (*d*, *J* = 7.7)	C(3) (GlcA)	104.5	5.30 (*d*, *J* = 7.7)	C(3) (GlcA)
H–C(2)	74.7	3.94 (*dd*, *J* = 7.7, 8.3)	C(1) and C(3) (Xyl)	74.7	3.93 (*dd*, *J* = 7.7, 8.3)	C(3) and C(1) (Xyl)
H–C(3)	78.1	4.07 (*t*, *J* = 8.3)	C(4) and C(2) (Xyl)	78.0	4.06 (*t*, *J* = 8.3)	C(4) and C(2) (Xyl)
H–C(4)	70.2	4.08 (*dd*, *J* = 10.3, 8.3, 5.0)		70.2	4.08 (*ddd*, *J* = 10.3, 8.3, 5.0)	
CH_2(5)	66.8	3.63 (*t*, *J* = 11.0);	C(4), C(3), and C(1) (Xyl);	66.7	3.63 (*t*, *J* = 11.0);	C(4), C(3), and C(1) (Xyl);
		4.22 (*dd*, *J* = 11.0, 5.0)	C(4) and C(3) (Xyl)		4.23 (*dd*, *J* = 11.0, 5.0)	C(4) and C(3) (Xyl)
Gal						
H–C(1)	103.7	5.53 (*d*, *J* = 7.7)	C(3) (Gal), C(2) (GlcA)	103.7	5.53 (*d*, *J* = 7.7)	C(3) (Gal), C(2) (GlcA)
H–C(2)	73.1	4.44 (*dd*, *J* = 7.7, 9.6)	C(1) (Gal)	73.1	4.44 (*dd*, *J* = 7.7, 9.6)	C(1) (Gal)
H–C(3)	76.2	4.01 (*dd*, *J* = 9.6, 3.0)	C(6), C(4), and C(1) (Gal)	76.2	4.01 (*dd*, *J* = 9.6, 3.0)	C(6), C(4), and C(1) (Gal)
H–C(4)	69.6	4.55 (*d*, *J* = 3.0)		69.6	4.54 (*d*, *J* = 3.0)	C(2) and C(5) (Gal)
H–C(5)	74.9	4.14 (*dd*, *J* = 9.6, 3.0)	C(3) (Gal)	74.9	4.13 (*dd*, *J* = 9.6, 3.0)	C(3) (Gal)
H–C(6)	61.2	4.42–4.44 (*m*), 4.47–4.51 (*m*)	C(4), C(5), and C(3) (Gal)	61.2	4.40–4.42 (*m*), 4.47–4.51 (*m*)	C(4), C(5), and C(3) (Gal)

Scheme 1. *Acid Hydrolysis of* **2**



cm^{-1} (C=C), and 1039 cm^{-1} (C–O–C). Interestingly, acid hydrolysis of **2** gave the same results as that of **1**, *i.e.*, aglycon **3** was isolated after complete hydrolysis *via* **7** (*Scheme 1*). Furthermore, analysis of the NMR data (^{1}H- and ^{13}C-NMR, HSQC, and HMBC, see *Tables 1* and *2*) showed that **2** was very similar to **1**. The differences between **1** and **2** concerned the chemical shifts of the C-atoms of rings D and E, including the trisubstituted C=C bond at δ 122.1 and 142.1, suggesting the presence of a (17β)-configurated aglycon with a *cis* D/E ring junction [9][10]. A ROESY experiment (*Fig. 2*) confirmed this configuration (correlation H–C(17)/H–C(18)/H–C(30)). Further comparison of the NMR data of rings D and E of **2** with those of remangilones B [10], allowed to attribute to the aglycon of **2** the structure (3β)-3-hydroxy-28-norolean-12-ene-16,23-dione, named neogypsogenin B (**4**), *i.e.*, the C(17) epimer of neogypsogenin A (**3**). In addition, the detailed comparison of the NMR data of the sugar moieties of **2** and **1** revealed that they are identical (*Table 2*). Consequently, compound **2** was determined to be neogypsogenin B 3-*O*-[*O*-β-D-galactopyranosyl-(1 → 2)-[*O*-β-D-xylopyranosyl-(1 → 3)]-β-D-glucopyranosiduronic acid.

Since compounds **1**, **2**, **5**, and **6** with identical sugar sequences were all isolated from *Gypsophila oldhamiana*, we suggest that a possible biogenetic implication of **1** and **2** originates from **6** (*Scheme 2*).

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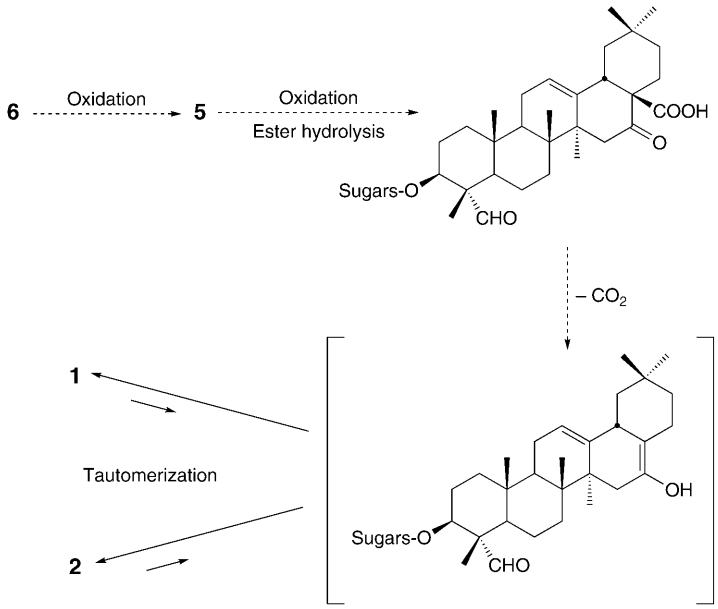
Scheme 2. *Postulated Biogenesis of* **1** *and* **2**



Experimental Part

General. TLC: pre-coated silica gel *60* F_{254} plates (*Qingdao Haiyang Chemical Co. Ltd.*; 0.25 mm, 200×200 mm for prep. TLC); detection by 10% H_2SO_4/EtOH for saponins and aniline/phthalate reagents for sugars. Column chromatography (CC): silica gel *H* (*Qingdao Haiyang Chemical Co. Ltd.*), *Sephadex LH-20* (*Pharmacia*), and *RP-C18* (40–63 μm; *FuJi*). Prep. HPLC: *Agilent-1100* apparatus with *Shim-park RP-18* column (Ø 2×20 cm). $[\alpha]_D$: *Jasco P-1020* polarimeter. IR Spectra (KBr): *Nicolet-Impact-410* spectrometer; $\tilde{\nu}$ in cm^{-1}. 1D- and 2D-NMR Spectra: *Bruker-ACF-500* instrument, at 300 K and 500 (^1H) and 125 MHz (^{13}C) with $SiMe_4$ as internal standard; δ in ppm, J in Hz. MS: *Agilent-1100-LC/MSD-Trap* (ESI-MS) and *Micro-Q-TOF* (HR-ESI-MS) spectrometer; in *m*/*z*.

Plant Material. The roots of *G. oldhamiana* (MIQ.) were collected in suburbs of Jinan, Shandong Province, China, in October 2004, and identified by Prof. *Yu-Yao Li* of the Department of Pharmacognosy, Shandong University. A voucher specimen (No. 041022) was deposited in the Department of Natural Medicinal Chemistry, China Pharmaceutical University.

Extraction and Isolation. The air-dried roots (30 kg) of *G. oldhamiana* were extracted with 70% EtOH/H_2O (3× 40 l, 2 h each for) under reflux. After evaporation, the residue was suspended in H_2O and partitioned between BuOH and H_2O. The BuOH-soluble portion (724 g) was fractionated by CC (silica gel; 100–200 mesh, $CHCl_3$/MeOH/H_2O 100:10:0 → 100:100:1): *Fr. 1–5*. Each fraction was further subjected to repeated CC (*RP-18*, MeOH/H_2O 4:6 → 8:2), and finally to CC (*Sephadex LH-20*, MeOH). *Fr. 3* yielded pure **6** (50 mg) and **1/2** (60 mg). The mixture **1/2** was purified by HPLC (MeCN/H_2O 60:40, UV detection at 210 nm, t_R 16.8 (**1**) and 18.0 min (**2**)): **1** (25 mg) and **2** (20 mg). *Fr. 4* yielded pure **5** (41 mg).

Neogypsoside A (=*(3β,17α)-16,23-Dioxo-28-norolean-12-en-3-yl* O-*β*-D-*Galactopyranosyl-(1 → 2)-[*O-*β*-D-*xylopyranosyl-(1 → 3)]-β*-D-*glucopyranosiduronic Acid*; **1**): White powder. $[\alpha]_D^{25} = -39.8$ (c = 0.13, MeOH). IR (KBr): 3439, 2939, 2860, 2750, 1709, 1628, 1386, 1078, 1041. ^1H-and ^{13}C-NMR (C_5D_5N): *Tables 1* and *2*. HR-ESI-MS: 933.4480 ($[M+Na]^+$, $C_{46}H_{70}O_{18}Na^+$; calc. 933.4460).

Neogypsoside B (=(3β)-16,23-Dioxo-28-norolean-12-en-3-yl O-*β*-D-*galactopyranosyl-(1 → 2)-[*O-*β*-D-*xylopyranosyl-(1 → 3)]-β*-D-*glucopyranosiduronic Acid*; **2**): White powder. $[\alpha]_D^{25} = +28.7$ ($c = 0.13$, MeOH). IR (KBr): 3429, 2924, 2860, 2750, 1707, 1632, 1388, 1039. ^{1}H- and ^{13}C-NMR (C_5D_5N): *Tables 1* and *2*. HR-ESI-MS: 933.4448 ($[M+Na]^+$, $C_{46}H_{70}O_{18}Na^+$; calc. 933.4460).

Acid Hydrolysis of **1** *and* **2**. Each compound (15 mg) was heated for 3 h in 2% H_2SO_4 in MeOH/H_2O 1:1 (10 ml) at 90° in a water bath. After evaporation of the MeOH, the aq. phase was extracted with CH_2Cl_2 (3×10 ml), the extract washed with H_2O, dried (Na_2SO_4), and evaporated, and the residue purified by CC (silica gel, $CHCl_3$/MeOH 15:1): **7** (7 mg from **1**, 6 mg from **2**). The acid aq. layer was neutralized with $BaCO_3$, filtered, evaporated. Xylose and galactose were identified with authentic samples by TLC (Me_2CO/BuOH/H_2O 5:4:1). The sugars were separated by prep. TLC (Me_2CO/BuOH/H_2O 5:4:1): D-xylose (2.5 mg; $[\alpha]_D^{25} = +18.1$ ($c = 0.15$, H_2O)) and D-galactose (2.0 mg; $[\alpha]_D^{25} = +58.1$ ($c = 0.15$, H_2O)).

*(Neogypsogenin-A-3-yl) β-*D-*Glucopyranosiduronic Acid Methyl Ester* (*=(3β,17α)-16,23-Dioxo-28-norolean-12-en-3-yl β-*D-*glucopyranosidfuronic Acid Methyl Ester*; **7**): White powder. $[\alpha]_D^{25} = -34.9$ ($c = 0.10$, MeOH). ^{1}H-NMR (C_5D_5N): 0.69, 0.79, 0.80, 0.90, 1.02, 1.27 (6*s*, 6 Me); 2.08 (*d*, *J* = 15.5, 1 H–C(15)); 2.13 (*td*, *J* = 4.0, 10.1, H–C(17)); 2.28 (*td*, *J* = 4.0, 10.1, H–C(18)); 2.58 (*d*, *J* = 15.7, 1 H–C(15)); 3.69 (*s*, MeO); 4.11–4.15 (*m*, H–C(3)); 4.86 (*d*, *J* = 8.0); 3.93–4.50 (*m*, H–C(2′) to H–C(5′)); 5.47 (br. *s*, H–C(12)); 9.71 (*s*, CHO). ^{13}C-NMR (C_5D_5N): 214.9 (C(16)); 208.0 (C(23)); 172.0 (C(6′)); 144.1 (C(13)); 119.0 (C(12)); 106.7 (C(1′)); 83.5 (C(3)); 79.1 (C(5′)); 78.6 (C(3′)); 76.4 (C(2′)); 74.3 (C(4′)); 56.7 (C(4)); 53.4 (MeO); 51.1 (C(17)); 49.3 (C(5)); 48.8 (C(9)); 45.5 (C(15)); 44.3 (C(14)); 44.3 (C(19)); 40.4 (C(8)); 40.0 (C(1)); 39.1 (C(21)); 38.5 (C(18)); 37.7 (C(10)); 34.7 (C(29)); 33.9 (C(7)); 32.0 (C(20)); 26.9 (C(27)); 26.5 (C(2)); 26.1 (C(30)); 25.3 (C(11)); 24.8 (C(22)); 21.9 (C(6)); 18.1 (C(26)); 16.9 (C(25)); 11.6 (C(24)). ESI-MS: 631 ($[M+H]^+$).

Acid Hydrolysis of **7**. Compound **7** (10 mg) was heated in 5% H_2SO_4 in dioxane/H_2O 1:1 (5 ml) at 100° for 5 h. After evaporation of the dioxane, the aq. phase was extracted with CH_2Cl_2 (3×5 ml), the extract evaporated, and the residue subjected to CC (silica gel $CHCl_3$/MeOH 20:1): **3** (3mg). The acid aq. layer was neutralized with $BaCO_3$, filtered, and evaporated. TLC ($CHCl_3$/MeOH/H_2O 10:5:1) indicated the presence of D-glucuronic acid $[\alpha]_D^{25} = +25.6$ ($c = 0.15$, H_2O).

Neogypsogenin A (*=(3β,17α)-3-Hydroxy-28-norolean-12-ene-16,23-dione*; **3**): White powder. $[\alpha]_D^{25} = +5.9$ ($c = 0.10$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 0.83, 0.87, 0.94, 0.97, 1.00, 1.14 (6*s*, 6 Me); 2.04 (*d*, *J* = 15.7, 1 H–C(15)); 2.51 (*d*, *J* = 15.7, 1 H–C(15)); 3.76–3.78 (*m*, H–C(3)); 5.47 (br. *s*, H–C(12)); 9.71 (*s*, CHO). ^{13}C-NMR ($CDCl_3$): 212.9 (C(16)); 209.0 (C(23)); 142.1 (C(13)); 117.0 (C(12)); 71.9 (C(3)); 55.7 (C(4)); 49.2 (C(17)); 48.3 (C(5)); 47.5 (C(9)); 43.5 (C(15)); 42.4 (C(14)); 42.3 (C(19)); 39.6 (C(8)); 38.0 (C(1)); 37.0 (C(21)); 36.4 (C(18)); 36.0 (C(10)); 32.7 (C(29)); 32.4 (C(7)); 30.0 (C(20)); 26.5 (C(2)); 24.8 (C(27)); 24.1 (C(30)); 23.5 (C(11)); 22.8 (C(22)); 20.7 (C(6)); 16.1 (C(26)); 14.8 (C(25)); 10.4 (C(24)). ESI-MS: 441 ($[M+H]^+$).

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