New Acylated Oleanane and Lupane Triterpenes from *Gymnema sylvestre*

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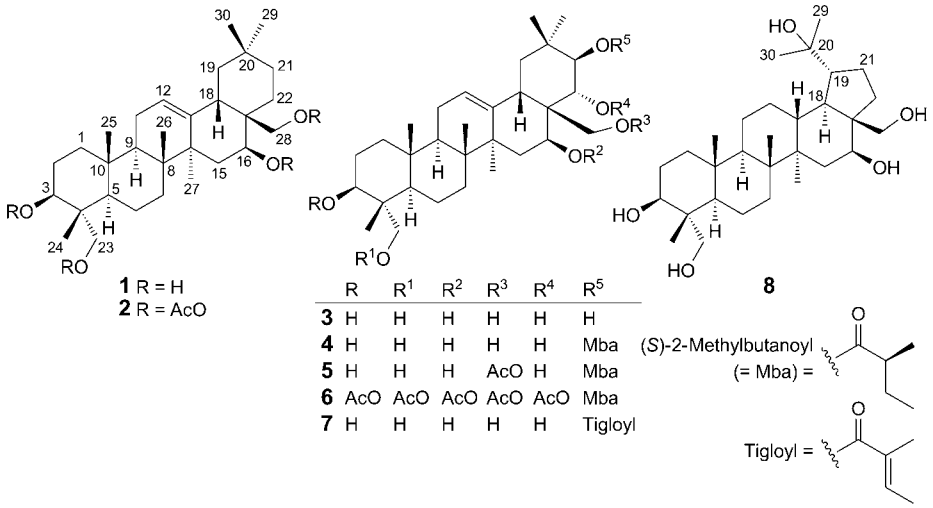
Phytochemical investigation of the aerial parts of *Gymnema sylvestre* led to the isolation of two known oleanane-type triterpenes, **1** and **3**, five new acylated derivatives, **2**, **4**, and **5**–**7**, and a new lupane-type triterpene, **8**. The structures and relative configurations of these compounds were elucidated by spectroscopic analyses, including 1D- and 2D-NMR spectroscopy and mass spectrometry, and by the comparison of their NMR data with those of related compounds.

Introduction. – *Gymnema sylvestre* (Asclepiadaceae), a vulnerable species, is a slow-growing, perennial woody climber in tropical and subtropical regions [1]. It is a potent antidiabetic plant and used in folk, ayurvedic, and homeopathic systems of medicine [2–5]. It is also used in the treatment of asthma, eye complaints, inflammations, family planning, and snake bite [6–9]. In addition, it possesses antimicrobial, antihypercholesterolemic [10], hepatoprotective [11], and sweet-suppressing activities [12]. It also acts as feeding deterrents to caterpillar, *Prodenia eridania* [13], prevents dental caries caused by *Streptococcus mutans* [14], and it is used in skin cosmetics [15]. The various reports on its multiple uses attracted attention for utilization of the plant for gynmemic acid (active principle). From the organic extract of *G. sylvestre*, we had isolated oleanane and lupane triterpenes [16]. In the continuing the investigation of *G. sylvestre*, we have isolated two known oleanane-type triterpenes, **1** and **3**, one obtained for synthesis, **2**, four new acylated derivatives, **4**–**7**, and a new lupane-type triterpene, **8**.

Results and Discussion. – Compound **1** was identified as (3β,16β)-olean-12-ene-3,16,23,28-tetrol by comparison of its spectral data with those in the literature [17].

Compound **2** had the molecular formula $C_{38}H_{58}O_8$ on the basis of the *quasi*-molecular-ion peak at *m*/*z* 643.4204 ($[M+H]^+$) in the HR-ESI-MS spectrum and ^{13}C-NMR data. The ^{1}H-NMR spectra (*Table 1*) revealed the presence of two O-bearing CH and two O-bearing CH_2 groups assigned by a HSQC experiment. The high chemical-shift values and the presence of four *singlet*s, at δ(H) 2.00 and 2.01, and 2.03 and 2.05 indicate that the carbinol functions are acetylated. The configurations of the O-bearing C-atoms have been deduced from a NOESY experiment, where the H-atom H–C(3) showed a NOE effect with the H-atoms of CH_2(23), and H-atoms of Me(24)



	R	R^1	R^2	R^3	R^4	R^5
3	H	H	H	H	H	H
4	H	H	H	H	H	Mba
5	H	H	H	AcO	H	Mba
6	AcO	AcO	AcO	AcO	AcO	Mba
7	H	H	H	H	H	Tigloyl

showed NOE effect with the H-atoms Me(25), indicating an α orientation for the CH_2(23) OR group. In the same experiment, H–C(16) showed NOE effect with the H-atoms Me(27), justifying a β orientation for the AcO group at C(16). All the spectral data completely defined the structure of compound **2** as (3β,16β)-olean-12-ene-3,16,23,28-tetrayl tetraacetate, already obtained from acetylation of the corresponding compound **1** and identified only by mass spectrometry [18].

Compound **3** was identified as (3β,16β,21β,22α)-olean-12-ene-3,16,21,22,23,28-hexol by comparison of its spectral data with those in the literature [19].

Compound **4** had the molecular formula $C_{35}H_{58}O_7$ based on the *quasi*-molecular-ion peak at *m*/*z* 591.4254 ($[M+H]^+$) in the HR-ESI-MS spectrum and ^{13}C-NMR data. The ^{1}H-NMR spectra (*Table 1*) revealed the presence of four O-bearing CH and two O-bearing CH_2 groups assigned by a HSQC experiment. The high chemical-shift value of H–C(21) (*doublet* at δ(H) 5.10) and the presence of signals assigned to a 2-methylbutanoyl unit (at δ(H) 2.44, 1.75–1.77, and 1.51–1.55, a Me *doublet* at δ(H) 1.18, and a Me *triplet* at δ(H) 0.96), indicate that the C(21) position is acylated. All the spectral data completely defined the structure of compound **4** as (3β,16β,21β,22α)-3,16,22,23,28-pentahydroxyolean-12-en-21-yl (2*S*)-2-methylbutanoate.

Compound **5** was identified as (3β,16β,21β,22α)-28-(acetyloxy)-3,16,22,23-tetrahydroxyolean-12-en-21-yl (2*S*)-2-methylbutanoate by comparison of its spectral data with those of the non-acylated triterpene **3**. It had the molecular formula $C_{37}H_{60}O_8$ on the basis of the *quasi*-molecular-ion peak at *m*/*z* 633.4360 ($[M+H]^+$) in the HR-ESI-MS spectrum and ^{13}C-NMR data. ^{1}H-NMR spectra (*Table 1*) revealed the presence of four O-bearing CH and two O-bearing CH_2 groups assigned by a HSQC experiment. The high chemical-shift value of H–C(21) (*doublet* at δ(H) 5.21), the presence of signals assigned to a 2-methylbutanoyl moiety (*multiplet*s at δ(H) 1.73–1.76, 1.53–1.56, a broad *quadruplet* at δ(H) 2.45, a Me *doublet* at δ(H) 1.18, and a Me *triplet* at δ(H) 0.96), and the correlation between H–C(21) and C(1′) (δ(C) 176.7), in the HMBC spectrum, indicated that C(21) was 2-methylbutanoylated. The chemical-shift values of

Table 1. *Selected ^{1}H-NMR Data of Compounds* **1**–**7** (at 500 MHz, in CD_3OD; δ(H) in ppm, *J* in Hz)

H-Atom	**1**	**2**[a])	**3**	**4**	**5**[a])	**6**[a])	**7**	**8**
H–C(3)	3.62 (*dd*, *J* = 10.8, 4.7)	4.75 (*dd*, *J* = 11.7, 4.9)	3.62 (*dd*, *J* = 11.3, 4.7)	3.61 (*dd*, *J* = 12.5, 4.0)	3.64 (br. *t*, *J* = 7.5)	4.77 (*dd*, *J* = 11.5, 4.7)	3.60 (*dd*, *J* = 10.0, 4.2)	3.59 (*dd*, *J* = 11.4, 5.0)
H–C(12)	5.22–5.27 (*m*)	5.26 (br. *t*, *J* = 2.8)	5.34 (br. *t*, *J* = 3.4)	5.38 (br. *t*, *J* = 3.3)	5.30–5.35 (*m*)	5.38–5.40 (*m*)	5.38–5.42 (*m*)	1.63–1.65 (*m*), 1.58–1.61 (*m*)
H–C(16)	4.26 (*dd*, *J* = 12.0, 5.0)	5.51 (*dd*, *J* = 12.2, 5.4)	4.61 (*dd*, *J* = 11.6, 5.8)	4.69 (*dd*, *J* = 10.8, 5.1)	4.72 (*dd*, *J* = 11.9, 5.1)	5.93 (*dd*, *J* = 11.8, 5.6)	4.80 (*dd*, *J* = 10.8, 5.0)	3.70 (*dd*, *J* = 11.8, 5.6)
H–C(21)			3.52 (*d*, *J* = 10.1)	5.10 (*d*, *J* = 10.5)	5.21 (*d*, *J* = 11.0)	5.17 (*d*, *J* = 11.1)	5.18 (*d*, *J* = 10.7)	1.29–1.33 (*m*)
H–C(22)			3.96 (*d*, *J* = 10.5)	4.14 (*d*, *J* = 10.5)	3.88 (*d*, *J* = 11.0)	5.44 (*d*, *J* = 11.1)	4.20 (*d*, *J* = 10.7)	2.25, (*dd*, *J* = 12.0, 6.9), 1.03–1.07 (*m*)
CH_2(23)	3.54 (*d*, *J* = 10.5), 3.31 (obs)	3.85 (*d*, *J* = 11.7), 3.66 (*d*, *J* = 11.7)	3.55 (*d*, *J* = 10.1), 3.29 (obs)	3.53 (*d*, *J* = 9.5), 3.30 (obs)	3.73 (*d*, *J* = 10.5), 3.42 (*d*, *J* = 11.0)	3.87 (*d*, *J* = 11.6), 3.72 (*d*, *J* = 11.6)	3.59 (*d*, *J* = 9.5), 3.30 (obs)	3.52 (*d*, *J* = 10.9), 3.30 (obs)
Me(24)	0.72 (*s*)	0.81 (*s*)	0.71 (*s*)	0.71 (*s*)	0.89 (*s*)	0.84 (*s*)	0.71 (*s*)	0.69 (*s*)
Me(25)	1.01 (*s*)	0.97[b]) (*s*)	1.01 (*s*)	1.02 (*s*)	0.97 (*s*)	0.93 (*s*)	1.03 (*s*)	0.91 (*s*)
Me(26)	1.04 (*s*)	0.98[b]) (*s*)	1.03 (*s*)	1.04 (*s*)	0.98 (*s*)	0.98 (*s*)	1.04 (*s*)	1.13 (*s*)
Me(27)	1.26 (*s*)	1.25 (*s*)	1.27 (*s*)	1.29 (*s*)	1.25 (*s*)	1.30 (*s*)	1.30 (*s*)	1.05 (*s*)
CH_2(28)	3.86 (*d*, *J* = 10.5), 3.26 (*d*, *J* = 11.0)	4.08 (*d*, *J* = 11.0), 3.98 (*d*, *J* = 11.0)	3.91 (*d*, *J* = 10.9), 3.51 (*d*, *J* = 10.1)	3.93 (*d*, *J* = 11.5), 3.59 (*d*, *J* = 11.5)	4.12 (*d*, *J* = 11.0), 4.61 (*d*, *J* = 11.2)	4.26 (*d*, *J* = 11.3), 3.92 (*d*, *J* = 11.3)	3.95 (*d*, *J* = 11.6), 3.57 (*d*, *J* = 11.6)	4.13 (*d*, *J* = 11.1), 3.36 (obs)
Me(29)	0.91 (*s*)	0.89 (*s*)	0.99 (*s*)	0.88 (*s*)	0.89 (*s*)	0.99 (*s*)	0.86 (*s*)	1.12 (*s*)
Me(30)	0.93 (*s*)	0.89 (*s*)	0.91 (*s*)	1.00 (*s*)	0.89 (*s*)	1.08 (*s*)	1.02 (*s*)	1.21 (*s*)
MeCO		2.00 (*s*), 2.01 (*s*), 2.03 (*s*), 2.05 (*s*)			2.12 (*s*)	1.92 (*s*), 2.02 (*s*), 2.04 (*s*), 2.06 (*s*), 2.10 (*s*)		
H–C(2′)				2.44 (br. *q*, *J* = 6.3)	2.45 (br. *q*, *J* = 6.5)	2.30 (br. *q*, *J* = 6.3)		
CH_2(3′)				1.75–1.77 (*m*), 1.51–1.55 (*m*)	1.73–1.76 (*m*), 1.53–1.56 (*m*)	1.66–1.71 (*m*), 1.41–1.44 (*m*)	6.86 (*q*, *J* = 8.0)	
Me(4′)				0.96 (*t*, *J* = 7.0)	0.96 (*t*, *J* = 7.1)	0.89 (*t*, *J* = 6.8)	1.83 (*d*, *J* = 8.0)	
Me(5′)				1.18 (*d*, *J* = 6.5)	1.18 (*d*, *J* = 7.0)	1.09 (*d*, *J* = 7.0)	1.87 (*s*)	

[a]) In $CDCl_3$. [b]) Values with the same superscripts are interchangeable.

CH_2(28) (*doublet*s at δ(H) 4.12 and 4.61), the presence of the signal assigned to AcO (*singlet* at δ(H) 2.12), and the correlation between CH_2(28) and the carboxy C-atom (δ(C) 171.3), in the HMBC spectrum indicated that C(28) position was acetylated.

Compound **6** had molecular formula $C_{45}H_{68}O_{12}$ based on *quasi*-molecular-ion peak at *m*/*z* 801.4782 ($[M+H]^+$) in the HR-ESI-MS spectrum and ^{13}C-NMR data. The ^{1}H-NMR spectra (*Table 1*) revealed the presence of four O-bearing CH and two O-bearing CH_2 groups, assigned by a HSQC experiment. The high chemical-shift values of the carbinol H-atoms, the presence of signals assigned to the 2-methylbutanoyl moiety (*multiplet*s at δ(H) 1.66 – 1.71, 1.41 – 1.44, a broad *quadruplet* at δ(H) 2.30, a Me *doublet* at δ(H) 1.09, and a Me *triplet* at δ(H) 0.89), and the presence of five *singlet*s at δ(H) 1.92, 2.02, 2.04, 2.06, and 2.10, indicated that the carbinol functions were acetylated, and that C(21) was acylated. All the spectral data completely defined the structure of compound **6** as (3β,16β,21β,22α)-3,16,22,23,28-pentakis(acetyloxy)olean-12-en-21-yl (2*S*)-2-methylbutanoate.

Compound **7** had molecular formula $C_{35}H_{56}O_7$ as deduced from the *quasi*-molecular-ion peak at *m*/*z* 589.4099 ($[M+H]^+$) in the HR-ESI-MS spectrum and ^{13}C-NMR data. The ^{1}H-NMR spectra (*Table 1*) revealed the presence of four O-bearing CH and two O-bearing CH_2 groups assigned by a HSQC experiment. The high chemical-shift value of H–C(21) (*doublet* at δ(H) 5.18) and the presence of signals assigned to a tigloyl moiety (broad *quadruplet* at δ(H) 6.86, a *doublet* Me at δ(H) 1.83, and a Me *singlet* at δ(H) 1.87) indicate that C(21) was acylated. All the spectral data completely defined the structure of compound **7** as (3β,16β,21β,22α)-3,16,22,23,28-pentahydroxyolean-12-en-21-yl (2*E*)-2-methylbut-2-enoate, previously reported as product of the acid hydrolysis of the aesculioside A isolated from *Aesculus chinensis* [20].

Compound **8** was isolated as an amorphous solid. The molecular formula $C_{30}H_{52}O_5$ (five degrees of unsaturation) was deduced from the *quasi*-molecular-ion peak at *m*/*z* 493.3886 ($[M+H]^+$) in the HR-ESI-MS. The IR spectrum showed absorptions at 3590, 3433 (OH) cm^{-1}. The ^{13}C-NMR spectrum exhibited 27 signals ascribed by DEPT and HSQC spectra to six Me, eleven CH_2 (two of them O-bearing), and seven CH groups (two of them O-bearing), and six quaternary C-atoms (one hydroxylated). These data suggested that **8** was a pentacyclic triterpene. The ^{1}H-NMR signals, together with those derived from an HSQC experiment, showed two CH_2 signals as two *doublet*s each at δ(H) 4.13, 3.36, and 3.52, 3.30, correlated to the C-atom signals at δ(C) 62.5 and 68.0, respectively, and two H-atom signals as *double doublet*s (δ(H) 3.70 and 3.59), correlated to the C-atom signals at δ(C) 79.8 and 74.4, respectively. In the upfield region, six Me *singlet*s (δ(H) 1.21, 1.13, 1.12, 1.05, 0.91, and 0.69), correlated in the HSQC to the C-atom signals at δ(C) 31.8, 17.2, 25.9, 17.2, 17.6, and 13.0, respectively (*Table 2*), were observed. The HMBC experiment provided useful data to elucidate the structure. CH Signal at δ(H) 3.59 and CH_2 signals at δ(H) 3.52, 3.30 gave cross-peaks with the C-atom signals at δ(C) 49.2, 43.8, and 13.0 assigned to C(5), C(4), and C(24), respectively. The CH signal at δ(H) 3.70 and CH_2 signals at δ(H) 4.13, 3.36 gave cross-peaks with the signal of C(22) at δ(H) 33.3, and with the signals at δ(C) 51.3 and 48.8, assigned to C(18) and C(17), respectively. Finally, both the Me signals at δ(H) 1.21 and 1.12 gave cross-peaks with the C-atom signals at δ(C) 53.3 and 74.6 assigned to C(19) and C(20), respectively. These data were in accordance with a structure of a lupane

Table 2. *^{13}C-NMR Data of Triterpenes* **1**–**8** (at 125 MHz, in CD_3OD; δ(C) in ppm)

C-Atom	**1**	**2**[a])	**3**	**4**	**5**[a])	**6**[a])	**7**	**8**
1	40.1	37.9	39.6	40.1	38.4	37.9	40.1	40.3
2	27.9	22.9	27.7	27.9	26.8	27.2	28.3	28.1
3	74.3	74.4	73.9	74.2	76.2	74.3	74.3	74.4
4	43.7	40.4	42.8	41.6	42.5	43.2	43.2	43.8
5	48.6	47.7	47.7	47.9	46.8	46.7	49.0 (obs)[b])	49.2
6	19.6	17.8	19.1	19.5	18.4	16.8	20.3	19.6
7	33.7	32.1	33.2	33.7	32.4	32.0	33.8	35.7
8	41.5	39.9	41.1	41.6	42.0	41.4	38.8	44.0
9	48.9	46.8	47.7	48.6	49.6	47.7	48.0	51.8
10	38.2	36.5	37.7	38.2	42.4	36.3	40.1	38.5
11	25.1	23.6	24.7	25.2	23.6	23.6	25.2	23.0
12	124.3	123.4	125.1	125.9	124.6	124.7	126.0	25.9
13	144.8	141.7	142.6	142.7	140.4	139.4	142.0	37.4
14	45.1	43.2	43.5	43.2	45.8	45.0	43.2	46.0
15	37.1	31.5	37.2	36.7	35.5	33.0	36.8	39.3
16	68.2	68.6	69.3	69.4	67.3	67.0	69.6	79.8
17	42.0	39.6	47.0	44.0	45.8	46.7	47.4	48.8
18	45.5	43.0	43.1	43.4	42.3	42.9	43.8	51.3
19	48.3	46.1	47.3	47.4	45.6	44.5	47.4	53.3
20	32.2	30.6	36.0	37.6	36.0	36.8	38.2	74.6
21	35.2	33.5	78.1	80.2	77.4	74.5	80.7	31.8
22	26.6	23.5	73.7	72.3	75.4	70.5	72.4	33.3
23	67.8	65.2	67.2	67.6	71.4	65.0	67.8	68.0
24	13.2	13.1	12.7	13.2	11.4	13.1	14.9	13.0
25	17.0	15.9	16.4	17.0	16.6	16.0	17.0	17.6
26	17.9	16.8	17.4	17.9	16.8	16.5	18.0	17.2
27	28.0	26.8	27.4	28.5	26.7	26.5	27.9	17.2
28	69.6	66.3	59.2	59.2	62.3	60.8	59.0	62.5
29	34.2	32.8	30.1	30.3	29.2	29.0	30.2	25.9
30	24.8	23.5	18.7	20.8	19.2	19.7	19.6	31.8
*Me*CO		20.8, 21.0, 2×21.2			20.8	19.6, 21.0, 2×21.2, 21.3		
Me*C*O		170.4, 170.6, 170.9, 171.1			171.3	168.6, 168.8, 168.9, 170.9, 171.1		
1′				177.0	176.7	176.6	169.0	
2′				43.8	41.6	40.5	128.0	
3′				28.2	27.4	26.5	138.8	
4′				12.5	11.5	11.7	14.9	
5′				17.5	15.8	17.7	17.0	

[a]) In $CDCl_3$. [b]) obs, Obscured by the solvent.

triterpene. They allowed us to determine the structure as (3β,16β)-lupane-3,16,20,23,28-pentol for this compound.

The configurations of the O-bearing C-atoms of all compounds have been defined by NOESY experiments as described for compound **2**.

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Experimental Part

General. HPLC: *Shimadzu LC-10AD* with a refractive-index detector *Shimadzu RID-10A*. Semiprep. HPLC: *RP-18* (*LiChrospher* 10 μm, 250 × 10 mm i.d., *Merck*) column with a flow rate of 1.2 ml min^{-1}. Column chromatography (CC): *Merck Kieselgel 60* (SiO_2; 230–400 mesh). Prep. TLC: silica gel (*UV-254* precoated) plates with 0.5- and 1.0-mm thickness (*Merck*). Optical rotations: in MeOH or CH_2Cl_2, with a *Perkin-Elmer 141* polarimeter. IR Spectra: *Jasco FT/IR-430* instrument. ^{1}H- and ^{13}C-NMR Spectra: *Varian INOVA-500* FT NMR spectrometer (at 499.710 and 125.663 MHz for ^{1}H and ^{13}C, resp.), in $CDCl_3$ or CD_3OD solns, at 25°, δ in ppm, J in Hz.

Plant Material. Gymnema sylvestre was purchased from *Mother Herbs Ltd.* (13 Street, Madhu Vihar, Patpadganj, Delhi – 110092, India, e-mail: info@motherherbs.com) and identified by Prof. *Antonino Pollio* of the Dipartimento delle Scienze Biologiche of the University of Naples. A sample specimen (HERBNAWY 124) has been deposited with the herbarium of the University Federico II.

Extraction and Isolation. Dried and finely powdered aerial parts of *G. sylvestre* (7.0 kg) were sliced and extracted with H_2O (25 l for 24 h) and successively with CH_2Cl_2 (20 l for 96 h). The org. extract was filtered and evaporated *in vacuo* to remove CH_2Cl_2. The resulting extract (350 g) was fractionated into acidic and neutral fractions with aq. 2N NaOH soln. The neutral soln., washed with H_2O and concentrated *in vacuo* (175 g), was subjected to CC (SiO_2; petroleum ether (PE), CH_2Cl_2, AcOEt, Me_2CO, MeOH, and H_2O).

The fraction eluted with AcOEt (20.0 g) was purified by CC (SiO_2; CH_2Cl_2/MeOH 100:0 to 0:100).

The fractions eluted with CH_2Cl_2 (913 mg) were purified by flash CC (SiO_2), and then the fractions eluted with CH_2Cl_2/MeOH 24:1 (111 mg) were further subjected to HPLC (*RP-18*; MeOH/MeCN/H_2O 3:4:3) to yield **4** (12 mg).

The fractions eluted with CH_2Cl_2/MeOH 9:1 (2.28 g) were seperated by CC (SiO_2). The fractions eluted with $CHCl_3$/MeOH 47:3 (250 mg) were further purified by HPLC (*RP-18*; MeOH/MeCN/H_2O 1:7:2) to yield triterpene **3** (10 mg); while the fractions eluted with $CHCl_3$/MeOH 9:1 (293 mg) were further separated by HPLC (*RP-18*; MeOH/MeCN/H_2O 2:2:1) to yield triterpenes **1** and **5** (80 and 5 mg, resp.).

The fractions eluted with CH_2Cl_2/MeOH 17:3 (1.28 g) were purified by flash CC (SiO_2), and the fractions eluted with CH_2Cl_2/MeOH 9:1 (600 mg) were purified first by *RP-18 Sep–Pak* filter with MeOH/MeCN/H_2O 1:2:2 and then by HPLC (*RP-18*; MeOH/MeCN/H_2O 2:3:5) to yield **8** (3 mg).

The fractions eluted with CH_2Cl_2/MeOH 1:1 (6.3 g) were purified by CC (SiO_2), and the fractions eluted with CH_2Cl_2/MeOH 19:1 (420 mg) were further subjected to flash CC (SiO_2). The fractions eluted with PE/AcOEt 22:3 (195 mg) were finally purified by *RP-18 Sep–Pak* filter with MeOH/MeCN/H_2O 2:1:2 to yield **2** (78 mg); the fractions eluted with PE/AcOEt 87:13 (145 mg) were purified first by *RP-18 Sep–Pak* filter with MeOH/MeCN/H_2O 3:4:3 and then by HPLC (*RP-18*; MeOH/MeCN/H_2O 3:5:2) to yield **7** (5 mg); finally the fractions eluted with PE/AcOEt 1:1 (35 mg) were purified by HPLC (*RP-18*; MeOH/MeCN 1:1) to give **6** (4 mg).

(3β,16β)-Olean-12-ene-3,16,23,28-tetrol (**1**). Amorphous powder. $[\alpha]_D^{25} = -0.67$ ($c = 0.22$, MeOH). IR (film): 3345, 1132, 1077, 1038. ^{1}H- and ^{13}C-NMR (CD_3OD): see *Table 1* and *2*, resp. ESI-MS: 475.2 ($[M+H]^+$). HR-ESI-MS: 475.3780 ($[M+H]^+$, $C_{30}H_{51}O_4^+$; calc. 475.3782).

(3β,16β)-Olean-12-ene-3,16,23,28-tetrayl Tetraacetate (**2**). Amorphous powder. $[\alpha]_D^{25} = +50.0$ ($c = 0.23$, MeOH). IR (film): 3333, 1758, 1754, 1117, 1091, 1033. ^{1}H and ^{13}C-NMR (CD_3OD): see *Table 1* and *2*, resp. HR-ESI-MS: 643.4204 ($[M+H]^+$, $C_{38}H_{59}O_8^+$; calc. 643.4205).

(3β,16β,21β,22α)-Olean-12-ene-3,16,21,22,23,28-hexol (**3**). Amorphous powder. $[\alpha]_D^{25} = -1.2$ ($c = 0.19$, MeOH). IR (film): 3328, 1111, 1089, 1037. ^{1}H- and ^{13}C-NMR (CD_3OD): see *Table 1* and *2*, resp. HR-ESI-MS: 507.3678 ($[M+H]^+$, $C_{30}H_{51}O_6^+$; calc. 507.3680).

(3β,16β,21β,22α)-3,16,22,23,28-Pentahydroxyolean-12-en-21-yl (2S)-2-Methylbutanoate (**4**). Amorphous powder. $[\alpha]_D^{25} = +3.5$ ($c = 0.21$, MeOH). IR (film): 3370, 1747, 1118, 1096, 1046. ^{1}H- and ^{13}C-NMR (CD_3OD): see *Table 1* and *2*, resp. HR-ESI-MS: 591.4254 ($[M+H]^+$, $C_{35}H_{59}O_7^+$; calc. 591.4255).

(3β,16β,21β,22α)-28-(Acetyloxy)-3,16,22,23-tetrahydroxyolean-12-en-21-yl (2S)-2-Methylbutanoate (**5**). Amorphous powder. $[\alpha]_D^{25} = +16.5$ ($c = 0.22$, MeOH). IR (film): 3352, 1746, 1113, 1091, 1041. ^{1}H- and ^{13}C-NMR (CD_3OD): see *Table 1* and *2*, resp. HR-ESI-MS: 633.4360 ($[M+H]^+$, $C_{37}H_{61}O_8^+$; calc. 633.4361).

(3β,16β,21β,22α)-3,16,22,23,28-Pentakis(acetyloxy)olean-12-en-21-yl (2S)-2-Methylbutanoate (**6**). Amorphous powder. $[\alpha]_D^{25} = +2.5$ ($c = 0.21$, MeOH). IR (film): 3355, 1764, 1750, 1113, 1090, 1042. ^{1}H- and ^{13}C-NMR (CD_3OD): *Table 1* and *2*, resp. HR-ESI-MS: 801.4782 ($[M+H]^+$, $C_{45}H_{68}O_{12}^+$; calc. 801.4784).

(3β,16β,21β,22α)-3,16,22,23,28-Pentahydroxyolean-12-en-21-yl (2E)-2-Methylbut-2-enoate (**7**). Amorphous powder. $[\alpha]_D^{25} = +3.5$ ($c = 0.22$, MeOH). IR (film): 3352, 1725, 1113, 1093, 1041. ^{1}H- and ^{13}C-NMR (CD_3OD): see *Table 1* and *2*, resp. HR-ESI-MS: 589.4099 ($[M+H]^+$, $C_{35}H_{57}O_7^+$; calc. 589.4099).

(3β,16β)-Lupane-3,16,20,23,28-pentol (**8**). Amorphous powder. $[\alpha]_D^{25} = +6.0$ ($c = 0.22$, MeOH). IR (film): 3334, 1118, 1090, 1041. ^{1}H- and ^{13}C-NMR (CD_3OD): see *Table 1* and *2*, resp. HR-ESI-MS: 493.3886 ($[M+H]^+$, $C_{30}H_{53}O_5^+$; calc. 493.3888).

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