Two New Oleanane-type Triterpenoids from *Buddleja asiatica*

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Two new oleanane-type triterpenoids, 13,28-epoxy-23-hydroxy-11-oleanene-3-one (**1**) and 13,28-epoxy-21β,23-dihydroxy-11-oleanene-3-one (**2**), along with seven known compounds, have been isolated from the aerial parts of *Buddleja asiatica* Lour. All structures were elucidated by spectroscopic techniques (NMR, MS, UV, and IR).

Key words: *Buddleja asiatica*, Oleanane Triterpenoids, 13,28-Epoxy-23-hydroxy-11-oleanene-3-one, 13,28-Epoxy-21β,23-dihydroxy-11-oleanene-3-one, 13,28-Epoxy-3β,23-*O*-isopropylidene-11-oleanene

Introduction

About 100 species of Buddleja belonging to the family Bulldejaceae are distributed in tropical and subtropical regions of North America, Africa and Asia. 29 species have been found in China [1]. The flowers, leaves and roots of many of Buddleja sp. are used as folk medicine in some countries [2]. For example, *Buddleja globosa* is reported from Chile, where the leaves and flowers are used for washing wounds and treating ulcers [2]. '*Mi-meng-hua*', prepared from the flowers of *Buddleja officinalis*, is a traditional Chinese medicine used to treat conjunctival congestion and clustered nebulae [3], and roots, stems and leaves of *B. asiatica* named '*Qi-li-xiang*', have been used as a popular traditional Chinese medicine for the treatment of fever, ache, diarrhea and articular rheumatism [4]. About 20 oleanane-type triterpenoids and their glycosides were isolated from Buddleja sp. in previous studies [5 – 8]. Up to now, no triterpenoids or triterpenoid glycosides from *B. asiatica* Lour have been reported. In the present study, we report the isolation and structure determination of two new oleanane-type triterpenoids (**1** – **2**), along with the known compounds, 13,28-epoxy-3β,23-*O*-isopropylidene-11-oleanene (**3**), 13,28-epoxy-3β,23-dihydroxy-11-oleanene (**4**) [6, 9], 3β,23,28-trihydroxy-11α-methoxy-12-oleanene (**5**) [6, 9], maslinic acid (**6**) [10], β-amyrin (**7**) [11], oleanolic aldehyde (**8**) [12], and oleanolic acid (**9**) [12] from aerial parts of *B. asiatica*, respectively (Fig. 1). Compounds **4** and **5** have been detected as nature products for the first time.

Results and Discussion

Compound **1** was found to have a molecular formula of $C_{30}H_{46}O_3$ on the basis of the HRESIMS molecular ion at *m/z* = 477.3341 $[M + Na]^+$ (calcd. for $C_{30}H_{46}O_3Na$ 477.3344), accounting for eight degrees of unsaturation. The IR data showed the presence of a hydroxyl group (3452 cm^{-1}) and a carbonyl group (1688 cm^{-1}), which was also indicated by the ^{13}C NMR data at δ_C = 218.5 (s). In the ^1H NMR spectrum, signals were observed for two olefinic protons at δ_H = 5.85 (1H, d, J = 10.4 Hz) and 5.42 (1H, dd, J = 10.4, 3.2 Hz), two AB systems of methylene protons δ_H = 3.71 (1H, d, J = 6.4 Hz) and 3.26 (1H, d, J = 6.4 Hz); δ_H = 3.69 (1H, dd, J = 11.6, 7.2 Hz) and 3.42 (1H, dd, J = 11.6, 7.2 Hz), and six tertiary methyl groups at δ_H = 1.13 (3H, s), 1.11 (3H, s), 0.99 (3H, s), 0.95 (3H, s), 0.94 (3H, s), and 0.86 (3H, s). The ^{13}C NMR spectrum indicated 30 carbon signals, including six methyl groups (δ_C = 16.2, 17.2, 19.1, 19.3, 23.5, 33.6), eleven methylenes (δ_C = 18.3, 25.1, 25.5, 30.5, 30.7, 34.7, 35.0, 37.0, 38.6, 66.4, 76.9), five methines (δ_C = 48.4, 50.9, 52.4, 131.3, 131.4), and eight quaternary carbons (δ_C = 31.6, 36.0, 41.4, 41.4, 44.0, 52.4, 84.6, 218.5). On the basis of the above evidence,

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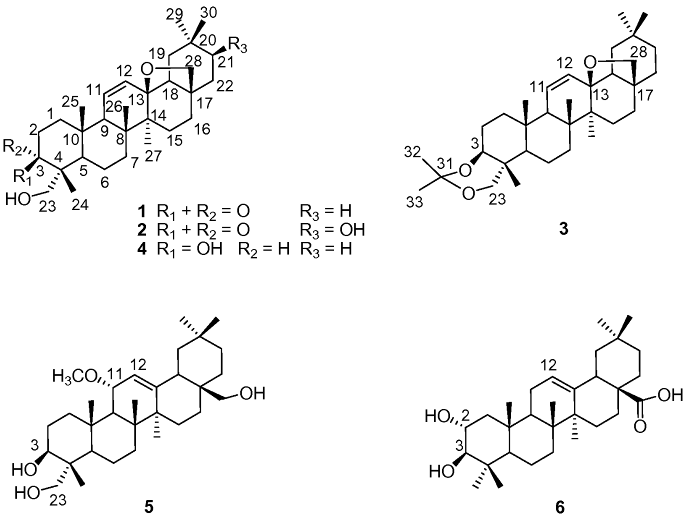

Fig. 1. Chemical structures of compounds **1** – **6**.

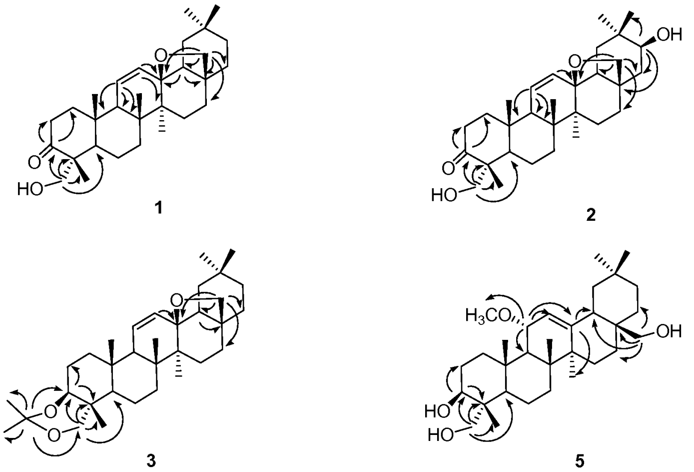

Fig. 2. Key HMBC correlations of compounds **1**, **2**, **3** and **5**.

compound **1** was concluded to be a triterpene based on the oleanane skeleton [9] with a double bond and six rings. One of those rings was an epoxide bridge between a methylene and a quaternary carbon. Comparison of NMR data with those of 13,28-epoxy-11-oleanene-3-one [13] showed that the two compounds were similar with the exception of an additional carbonyl function δ_C = 66.4 (t) and the absence of a methyl group in **1**. The proton signals at δ_H = 3.69 (1H, dd, *J* = 11.6, 7.2 Hz) and 3.42 (1H, dd, *J* = 11.6, 7.2 Hz) corresponding to δ_C = 66.4 (t) in its HSQC spectrum, showed cross peaks to δ_C = 218.5 (s, C-3), 52.4 (s, C-4), 48.4 (d, C-5), and 16.2 (q, C-24/23) in the HMBC spectrum, which suggested that oxygen substitution took place at C-23/24. However, in the ROESY spectrum, the correlation betweeen δ_H = 1.01 (3H, s, H-25) and δ_H = 0.99 (3H, s, H-24) indicated the hydroxy substitution at C-23. In the HMBC spectrum (Fig. 2), the oxygenated methylene protons at δ_H = 3.71 and 3.26 (each 1H, d, *J* = 6.4 Hz) corresponding to δ_C = 76.9 (t, C-28) in the HSQC spectrum, showed cross peaks to the quaternary carbon at δ_C = 84.6 (s, C-13). Moreover, C-13 was correlated with the olefinic proton signals at δ_H = 5.85 (H-12) and 5.42 (H-11), confirming the double bond at the C-11/12 position of the oleanane skeleton with the six-membered ring formed *via* an ether linkage between C-28 and C-13. Thus, compound **1** was elucidated as 13,28-epoxy-23-hydroxy-11-oleanene-3-one. All assignments of ^{1}H-, ^{13}C NMR of **1** were confirmed by a detailed analysis of HSQC, HMBC and ROESY spectra (Tables 1 and 2).

Table 1. ^{1}H NMR data of **1**, **2**, **3**, **5** in $CDCl_3$ solution[a].

Position	**1**	**2**	**3**	**5**
1	2.10 (1H, m)	2.11 (1H, m)	1.92 (1H, m)	1.91 (1H, m)
	1.36 (1H, m)	1.29 (1H, m)	1.00 (1H, m)	1.25 (1H, m)
2	2.68 (1H, m)	2.72 (1H, m)	1.65 (1H, m)	1.59 (2H, m)
	2.30 (1H, m)	2.33 (1H, m)	1.47 (1H, m)	
3			3.51 (1H, dd, 11.6, 4.0)	3.63 (1H, brt, 9.0)
5	1.66 (1H, m)	1.67 (1H, m)	0.78 (1H, dd, 12.6, 1.8)	0.93 (1H, m)
6	1.65 (1H, m)	1.67 (1H, m)	1.55 (1H, m)	1.40 (2H, m)
	1.44 (1H, m)	1.46 (1H, m)	1.18 (1H, m)	
7	1.25 (1H, m)	1.47 (1H, m)	1.29 (1H, m)	1.46 (1H, m)
	1.27 (1H, m)	1.30 (1H, m)	1.18 (1H, m)	1.25 (1H, m)
9	1.97 (1H, brs)	1.98 (1H, brs)	1.88 (1H, brs)	1.70 (1H, m)
11	5.42 (1H, dd, 10.4, 3.2)	5.44 (1H, dd, 10.3, 2.7)	5.37 (1H, dd, 10.3, 3.0)	3.80 (1H, dd, 8.5, 3.0)
12	5.85 (1H, d, 10.4)	5.88 (1H, d, 10.3)	5.83 (1H, d, 10.3)	5.34 (1H, d, 3.0)
15	1.76 (1H, m)	1.82 (1H, m)	2.01 (1H, m)	1.60 (1H, m)
	0.98 (1H, m)	1.00 (1H, m)	1.10 (1H, m)	0.98 (1H, m)
16	2.00 (1H, m)	1.98 (1H, m)	1.78 (1H, m)	1.88 (1H, m)
	1.12 (1H, m)	1.30 (1H, m)	0.98 (1H, m)	1.17 (1H, m)
18	1.66 (1H, m)	1.70 (1H, m)	1.65 (1H, m)	2.02 (1H, dd, 13.5, 4.0)
19	1.71 (1H, m)	1.69 (1H, m)	1.72 (1H, m)	1.70 (1H, m)
	1.27 (1H, m)	1.42 (1H, m)	1.25 (1H, m)	1.17 (1H, m)
21	1.35 (1H, m)	3.59 (1H, dd, 11.5, 4.0)	1.34 (1H, m)	1.30 (1H, m)
	1.19 (1H, m)		1.22 (1H, m)	1.17 (1H, m)
22	1.48 (1H, m)	1.70 (1H, m)	1.46 (1H, m)	1.51 (1H, m)
	1.45 (1H, m)	1.46 (1H, m)	1.44 (1H, m)	1.37 (1H, m)
23	3.69 (1H, dd, 11.6, 7.2)	3.72 (1H, dd, 11.0, 6.5)	3.53 (1H, d, 10.8)	3.71 (1H, d, 10.0)
	3.42 (1H, dd, 11.6, 7.2)	3.43 (1H, dd, 11.0, 6.5)	3.44 (1H, d, 10.8)	3.41 (1H, d, 10.0)
24	0.99 (3H, s)	1.01 (3H, s)	1.04 (3H, s)	0.89 (3H, s)
25	1.11 (3H, s)	1.13 (3H, s)	0.94 (3H, s)	1.07 (3H, s)
26	1.13 (3H, s)	1.14 (3H, s)	1.07 (3H, s)	0.96 (3H, s)
27	0.94 (3H, s)	0.95 (3H, s)	0.94 (3H, s)	1.22 (3H, s)
28	3.71 (1H, d, 6.4)	3.72 (1H, d, 6.5)	3.70 (1H, d, 6.8)	3.50 (1H, d, 11.0)
	3.26 (1H, d, 6.4)	3.32 (1H, d, 6.5)	3.25 (1H, d, 6.8)	3.18 (1H, d, 11.0)
29	0.95 (3H, s)	1.05 (3H, s)	0.86 (3H, s)	0.89 (3H, s)
30	0.86 (3H, s)	0.87 (3H, s)	0.96 (3H, s)	0.89 (3H, s)
32			1.44 (3H, s)	
33			1.42 (3H, s)	
CH_3O-				3.21 (3H, s)

[a] Spectra recorded at 400 MHz (**1** and **3**) or 500 MHz (**2** and **5**); δ in ppm, J in Hz.

Compound **2** showed a molecular ion peak at m/z = 493.3310 $[M + Na]^+$ in the HRESIMS. Its IR data indicated the presence of two hydroxyl groups (3481 cm^{-1} and 3418 cm^{-1}) and a carbonyl group (1687 cm^{-1}). According to the ^{1}H, ^{13}C NMR spectra (Tables 1 and 2), compound **2** was similar to **1** besides of the presence of a methine group (δ_C = 74.5, d) and the lack of a methylene group in **2**. In the HSQC spectrum, an oxygenated methine proton signal at δ_H = 3.59 (1H, dd, J = 11.5, 4.0 Hz) corresponding to δ_C = 74.5 (d), showed correlation with the carbon signals at δ_C = 43.7 (s, C-17), 39.2 (t, C-22), 17.3 (q, C-30), and 29.7 (q, C-29), suggesting that the signal was to be attributed to H-21. In the ROESY spectrum, the correlation betweeen H-18β (δ_H = 1.70, 1H) and δ_H = 1.42 (H-19, m, 1H) indicated that the latter was in a β-orientation, so the other proton δ_H = 1.69 (m, 1H) at the same carbon was in an α-orientation. Furthermore, the hydroxyl group at C-21 was stationed in a β-orientation according to ROESY correlations of H-19α/H-21. So **2** was identified as 13,28-epoxy-21β,23-dihydroxy-11-oleanene-3-one.

Compound **3** showed the molecular formula $C_{33}H_{52}O_3$, as evidenced by the HRESIMS data. Its IR spectrum displayed no absorptions due to hydroxyl and carbonyl groups. ^{1}H, ^{13}C NMR, DEPT spectra of **3** displayed similarities to those of compound **4** besides three additional carbons [δ_C = 98.8 (s), 19.4 (q), 29.8 (q)]. In addition, the carbon signal at δ_C = 98.8 (s) showed cross peaks to H-3 (1H, δ_H = 3.51) and H-23 (2H, δ_H = 3.53, 3.44), and to two tertiary methyl groups (δ_H = 1.42, 1.44), indicating an additional quaternary carbon of an isopropylidene unit connected to C-3, C-23 by an oxygen bridge. This presumption could be confirmed by the HMBC spectrum. The large coupling con-

Table 2. ^{13}C NMR data of **1**–**5** in $CDCl_3$ solution[a].

Position	**1**	**2**	**3**	**4**	**5**
1	38.6 (t)	38.7 (t)	38.6 (t)	37.8 (t)	39.1 (t)
2	35.0 (t)	35.0 (t)	23.4 (t)	26.0 (t)	27.0 (t)
3	218.5 (s)	218.0 (s)	77.3 (d)	75.9 (d)	76.4 (d)
4	52.4 (s)	52.7 (s)	37.0 (s)	41.3 (s)	41.9 (s)
5	48.4 (d)	48.6 (d)	51.1 (d)	49.1 (d)	49.7 (d)
6	18.3 (t)	18.3 (t)	17.0 (t)	17.5 (t)	18.5 (t)
7	30.5 (t)	30.6 (t)	30.7 (t)	30.6 (t)	33.1 (t)
8	41.4 (s)	41.5 (s)	41.5 (s)	41.3 (s)	41.7 (s)
9	52.4 (d)	52.5 (d)	53.1 (d)	53.0 (d)	51.7 (d)
10	36.0 (s)	36.5 (s)	37.0 (s)	36.0 (s)	38.0 (s)
11	131.3 (d)	131.1 (d)	130.9 (d)	130.5 (d)	75.8 (d)
12	131.4 (d)	131.5 (d)	131.7 (d)	132.2 (d)	122.0 (d)
13	84.6 (s)	84.3 (s)	84.6 (s)	84.9 (s)	148.6 (s)
14	44.0 (s)	43.5 (s)	43.7 (s)	43.6 (s)	43.0 (s)
15	25.1 (t)	25.2 (t)	25.2 (t)	25.0 (t)	25.6 (t)
16	25.5 (t)	26.9 (t)	25.5 (t)	25.4 (t)	21.8 (t)
17	41.4 (s)	43.7 (s)	41.4 (s)	41.3 (s)	36.7 (s)
18	50.9 (d)	50.3 (d)	51.0 (d)	50.9 (d)	41.7 (d)
19	37.0 (t)	36.0 (t)	36.9 (t)	36.9 (t)	46.1 (t)
20	31.6 (s)	36.6 (s)	31.6 (s)	31.5 (s)	30.9 (s)
21	34.7 (t)	74.5 (d)	35.0 (t)	34.7 (t)	34.0 (t)
22	30.7 (t)	39.2 (t)	30.7 (t)	30.8 (t)	30.9 (t)
23	66.4 (t)	66.5 (t)	72.4 (t)	70.7 (t)	71.8 (t)
24	16.2 (q)	16.2 (q)	11.8 (q)	10.8 (q)	11.4 (q)
25	17.2 (q)	17.1 (q)	19.2 (q)	18.0 (q)	17.2 (q)
26	19.1 (q)	19.1 (q)	19.4 (q)	19.1 (q)	18.1 (q)
27	19.3 (q)	19.2 (q)	19.2 (q)	19.3 (q)	25.1 (q)
28	76.9 (t)	76.3 (t)	76.9 (t)	76.7 (t)	69.6 (t)
29	33.6 (q)	29.7 (q)	33.6 (q)	33.5 (q)	32.9 (q)
30	23.5 (q)	17.3 (q)	23.5 (q)	23.4 (q)	23.5 (q)
31			98.9 (s)		
32			19.4 (q)		
33			29.8 (q)		
CH_3O-					53.8 (q)

[a] Spectra recorded at 100 MHz (**1**, **3** and **4**) or 125 MHz (**2** and **5**); δ in ppm; assignments are based on DEPT, HSQC and HMBC spectra.

stant of H-3 (J = 11.6, 4.0 Hz) indicated an α-orientation of H-3 [14]. Thus, compound **3** was elucidated as 13,28-epoxy-3β, 23-*O*-isopropylidene-11-oleanene.

Compound **3** should be an artificial product, since it was obtained from Me_2CO solutions of **4** kept at 50 °C for one hour but not in other solvents. Compounds **4** and **5** are aglycones of the mimengosides A and B [6], respectively. However, they have been detected for the first time as natural products [15, 16].

Tests of the biological activities of the new compounds have not been carried out as yet.

Experimental Section

General

Optical rotations were measured with a Horiba SPEA-300 spectropolarimeter. All melting points were measured on an XRC-1 apparatus and are uncorrected. 1D and 2D NMR spectra were recorded on Bruker AM-400 MHz and DRX-500 MHz NMR spectrometers with TMS as internal standard. ESI-MS and HRESIMS spectral data were obtained on an API Qstar Palsar I mass spectrometer. EI-MS spectra were run on a VG Autospec-3000 mass spectrometer. IR spectra were measured on a Brucker Tensor 27 spectrometer with KBr pellets. Rp-18 silica gel (40–65 μm) was bought from Merck, Germany. Silica gel (200–300 mesh) for column chromatography and GF_{254} for TLC were obtained from the Qindao Marine Chemical factory, Qindao, P. R. China. Compounds were detected under UV (254 nm and 365 nm) before and after spraying with an anisaldehyde sulfuric acid solution followed by heating.

Plant material

The aerial parts of *B. asiatica* Lour were collected in Guangxi Province, P. R. China, in July 2006 and identified by Mrs. Chun-Xia Zeng, Kunming Institute of Botany, Chinese Academy of Sciences. A voucher specimen has been deposited in the Herbarium of the Department of Taxonomy, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and isolation

Air-dried aerial parts (12.5 kg) were crushed and extracted with 90 % aqueous MeOH (40 L × 4) at r. t. (48 h × 4). After removal of the MeOH under reduced pressure, the viscous residue was partitioned with EtOAc (10 L × 4) to afford EtOAc and H_2O extracts. The EtOAc fraction (218 g) was chromatographed on a prepacked silica gel (2.0 kg, 200–300 mesh) column, using a mixture of $CHCl_3$ and Me_2CO [from $CHCl_3$-Me_2CO (1 : 0) to $CHCl_3$-Me_2CO (1 : 1)], to give nine fractions (I–IX). Fraction IV (12.0 g) was submitted to silica gel (300 g) and eluted with petroleum ether-Me_2CO (15 : 1, 10 : 1, 8 : 1, 5 : 1), to yield subfractions A–D. Subfraction B was purified on Sephadex LH-20 ($CHCl_3$: MeOH = 1 : 1), to yield compound **4** (8.7 mg). Subfraction C was purified by silica gel and eluted with petroleum ether-EtOAc to offord compound **1** (57.5 mg). Subfraction D was applied on RP-18 using MeOH-H_2O, to give compounds **7** (51.3 mg) and **8** (33.6 mg). Fraction V (16.0 g) was submitted to silica gel (400 g) and eluted with petroleum ether-EtOAc (8 : 1, 4 : 1, 2 : 1), to give subfractions E–G. Subfraction E was purified by recrystallization from cold Me_2CO to give compound **2** (12.6 mg). Subfraction F was first applied on RP-18 using MeOH-H_2O and then Sephadex LH-20 ($CHCl_3$: MeOH = 1 : 1), to give compounds **5** (30.2 mg), **3** (162.7 mg) and **9** (58.3 mg). Subfraction G was first applied on silica gel using $CHCl_3$-Me_2CO and then purified by recrystallization from cold MeOH to give compound **6** (167.9 mg).

13,28-Epoxy-23-hydroxy-11-oleanene-3-one (**1**)

White needles (CH_3COCH_3). – M. p. 204 – 206 °C. – $[\alpha]_D^{22}$ = +23.4 ($CHCl_3$, c = 0.47). – IR (KBr): ν = 3452 (OH), 2915, 1688 (CO) cm^{-1}. – MS ((+)-ESI): *m/z* = 455 $[M+1]^+$. – HRMS ((+)-ESI): *m/z* = 477.3341 (calcd. 477.3344 for $C_{30}H_{46}O_3Na^+$, $[M+Na]^+$). – ^1H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100 MHz, $CDCl_3$) spectral data see Tables 1 and 2, respectively.

13,28-Epoxy-21β,23-dihydroxy-11-oleanene-3-one (**2**)

White needles (CH_3COCH_3). – M. p. 221 – 222 °C. – $[\alpha]_D^{22}$ = +97.6 ($CHCl_3$, c = 0.07). – IR (KBr): ν = 3481 (OH), 3418 (OH), 2921, 2865, 1687 (CO) cm^{-1}. – MS (EI, 70 eV): *m/z* (%) = 470 (6) $[M]^+$, – 452 (3) $[M–H_2O]^+$. – HRMS ((+)-ESI): *m/z* = 493.3310 (calcd. 493.3293 for $C_{30}H_{46}O_4Na^+$, $[M+Na]^+$). – ^1H NMR (500 MHz, $CDCl_3$), and ^{13}C NMR (125 MHz, $CDCl_3$) spectral data see Tables 1 and 2, respectively.

13,28-Epoxy-3β,23-O-isopropylidene-11-oleanene (**3**)

White amorphous powder. – $[\alpha]_D^{22}$ = +62.5 ($CHCl_3$, c = 0.08). – MS ((+)-ESI): *m/z* = 497 $[M+1]^+$. – HRMS ((+)-ESI): *m/z* = 519.3800 (calcd. 519.3814 for $C_{33}H_{52}O_3Na^+$; $[M+Na]^+$). – ^1H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (100 MHz, $CDCl_3$) spectral data see Tables 1 and 2, respectively.

13,28-Epoxy-3β, 23-dihydroxy-11-oleanene (**4**)

White amorphous powder. – MS ((+)-ESI): *m/z* = 457 $[M+1]^+$. – ^1H NMR (400 MHz, $CDCl_3$): δ_H = 5.82 (1H, d, J = 10.4 Hz, H-12), 5.31 (1H, dd, J = 10.4, 3.0 Hz, H-11), 3.66 (1H, d, J = 5.4 Hz, H-28), 3.20 (1H, d, J = 5.4 Hz, H-28), 3.59 (1H, d, J = 10.5 Hz, H-23), 3.32 (1H, d, J = 10.5 Hz, H-23), 3.55 (1H, brt, J = 8.6 Hz, H-3), 1.02 (3H, s, H-26), 0.91 (3H, s, H-25), 0.89 (3H, s, H-24), 0.88 (3H, s, H-29), 0.82 (3H, s, H-27), 0.79 (3H, s, H-30). – ^{13}C NMR (100 MHz, $CDCl_3$) spectral data see Table 2.

3β,23,28-Trihydroxy-11α-methoxy-12-oleanene (**5**)

White needles (CH_3COCH_3). – M. p. 227 – 228 °C. – MS (EI, 70 eV): *m/z* (%) = 488 (11) $[M]^+$, 470 (6) $[M–H_2O]^+$, 456 (27) $[470–CH_3 + H]^+$, 425 (40) $[456–OCH_3]^+$. – ^1H NMR (500 MHz, $CDCl_3$), and ^{13}C NMR (125 MHz, $CDCl_3$) spectral data see Tables 1 and 2, respectively.

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