Oleanane-Type Triterpenes from the Flowers and Roots of *Saussurea muliensis*

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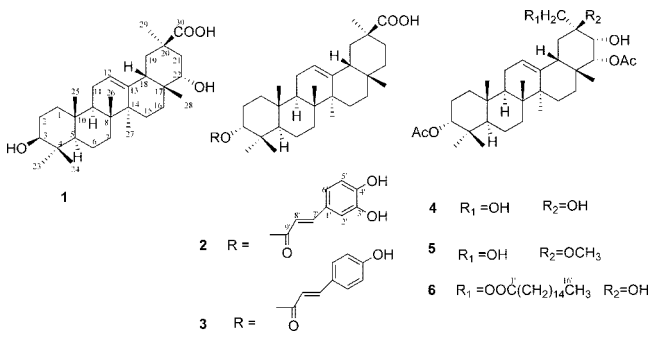
Six new oleanane-type triterpenes (**1**−**6**), along with five known compounds, were isolated from the flowers and roots of *Saussurea muliensis*. On the basis of spectroscopic methods, with special emphasis on 1D and 2D NMR techniques, the structures of the new compounds were characterized as 3*β*,22α-dihydroxyolean-12-en-30-oic acid (**1**), 3α-(*E*)-caffeoyloxyolean-12-en-30-oic acid (**2**), 3α-(*E*)-coumaroyloxyolean-12-en-30-oic acid (**3**), 3α,22α-diacetoxy-20*β*,21α,29-trihydroxy-30-norolean-12-ene (**4**), 3α,22α-diacetoxy-21α,29-dihydroxy-20*β*-methoxy-30-norolean-12-ene (**5**), and 3α,22α-diacetoxy-20*β*,21α-dihydroxy-29-palmityloxy-30-norolean-12-ene (**6**). The isolated compounds (**1**−**6**) were not active against *Staphylococcus aureus*, *Escherichia coli*, *Bacillus cereus*, and *Candida albicans*.

The genus *Saussurea* (family Asteraceae) contains more than 300 species distributed in the northern temperate zone of the world. Over 200 species of the genus are found in mainland China, more than 10 of which have long been used in Chinese folk medicine. Their use has proved to be efficacious in relieving internal heat or fever, harmonizing menstruation, invigorating blood circulation, stopping bleeding, alleviating pain, and increasing energy.[1,2] Pharmacological studies have shown that some *Saussurea* species possess activities such as scavenging of free radicals, in addition to having constituents that induce antifatigue, anti-inflammation, anticancer, and immunomodulation effects.[3–6] Previous chemical investigations of *Saussurea* species resulted in the isolation of various compounds, which included flavonoids, coumarins, lignans, sesquiterpene lactones, steroids, cardenolides, and triterpenes.[7–11] *S. muliensis* Hand.-Mazz., named "Muli Xue Lian" in traditional Chinese medicine, is a perennial herbaceous plant distributed in scree and stone meadows having elevations above 4300 m. Its phytochemical or pharmacological properties have not yet been reported. In this article, the isolation, structural elucidation, and the results of the antimicrobial activity assay of six new triterpenes (**1**−**6**), including three new 30-noroleanane-type compounds, are reported. It is worth noting that various types of pentacyclic triterpenes such as taraxastane, α-amyrin, and *β*-amyrin have been reported in this genus,[9,11,12] but 30-noroleanane-type nortriterpenes are new in this species. In addition, five previously known compounds have been readily identified as a mixture of *β*-sitosterol and stigmasterol (**7** and **8**),[12] 24-methylene-9,19-cyclolanostan-3-ol (**9**),[12] *p*-hydroxybenzoic acid (**10**),[13] and paprazine (**11**)[14] through analysis of their physical and spectroscopic data (IR, MS, and ^{1}H NMR).



Results and Discussion

A methanol extract of the flowers and roots (6.5 kg) of *S. muliensis* was successively extracted with petroleum ether (60−90 °C), EtOAc, and *n*-BuOH. By carrying out a series of column chromatographic separations, compounds **1** (10 mg), **2** (13 mg), **3** (3 mg), **4** (8 mg), **5** (9 mg), and **6** (36 mg) were obtained from the EtOAc extract, together with five previously known compounds (**7**−**11**).

The molecular formula of **1** was determined to be $C_{30}H_{48}O_4$ by the HRESIMS ion at *m/z* 471.3483 $[M - H]^-$ (calcd for $C_{30}H_{47}O_4$, 471.3480). The IR spectrum showed absorption bands corresponding to hydroxy (3424 cm^{-1}) and carboxylic (1698 and 2526 cm^{-1}) groups. The ^{13}C NMR and DEPT spectra showed 30 carbon resonances including seven tertiary methyls (*δ* 14.8, 15.1, 16.2, 24.1, 25.4, 27.5, and 27.9), nine methylenes, six methines (two oxymethines at *δ* 78.5 and 76.2, one olefinic at *δ* 122.9, and three sp^3 hybridized), and eight quaternary carbons (one carboxylic carbon at *δ* 179.9, one olefinic at *δ* 143.8, and six sp^3 hybridized). These data, when coupled with the information from the ^{1}H NMR spectrum [seven tertiary methyls (*δ* 0.79, 0.91, 0.97, 0.98, 1.00, 1.16, and 1.18), one olefinic proton at *δ* 5.27 (brs), and a pair of oxymethine protons at *δ* 3.15 and 3.36], indicated that compound **1** was based on a dihydroxyolean-12-enoic acid skeleton.[15–17]

The HMBC correlations of Me-23 (*δ* 0.98) and Me-24 (*δ* 0.79) to C-3 (*δ* 78.5), C-4 (*δ* 38.7), and C-5 (*δ* 55.5) were used to position a hydroxy group at C-3. Further analysis of the HMBC data showed that the other hydroxy group was attached to C-16 or C-22 as indicated by the correlations of Me-28 (*δ* 0.91) with C-16 or C-22 (*δ* 19.5), C-17 (*δ* 37.5), C-18 (*δ* 48.1), and C-22 or C-16 (*δ* 76.2). However, the oxymethine proton at *δ* 3.36 (1H, dd, $J = 12.4, 4.0$ Hz) showed correlations with C-20 (*δ* 43.4) and C-21 (*δ* 38.6), which indicated that the hydroxy group was located at C-22. Other HMBC data showed that the carboxy group was attached to C-20 of the ring E as evidenced by the correlations of a tertiary methyl at *δ* 1.16 with the carbonyl carbon (*δ* 179.9) of a carboxylic acid group and with C-19 (*δ* 42.4), C-20 (*δ* 43.4), and C-21 (*δ* 38.6). The ^{1}H NMR coupling constants [*δ* 3.15 (1H, dd, $J = 10.8, 5.2$ Hz, H-3) and *δ* 3.36 (1H, dd, $J = 12.4, 4.0$ Hz, H-22)] indicated a 3*β*,22α-dihydroxy arrangement, as in maytenfolic acid.[15–17] In an NOE experiment, irradiation of H-22 enhanced the CH_3-28 (3.56%) and H-21*β* (1.20%) resonances, without a signal increase of CH_3-29. All the evidence indicated that the structure of **1** is 3*β*,22α-dihydroxyolean-12-en-30-oic acid.

Compound **2** was assigned the molecular formula $C_{39}H_{54}O_6$, as derived from its HRESIMS data (*m/z* 641.3820 $[M + Na]^+$) in combination with the ^{13}C NMR and DEPT spectra. The IR spectrum indicated the presence of hydroxy (3389 cm^{-1}), carboxylic (1690

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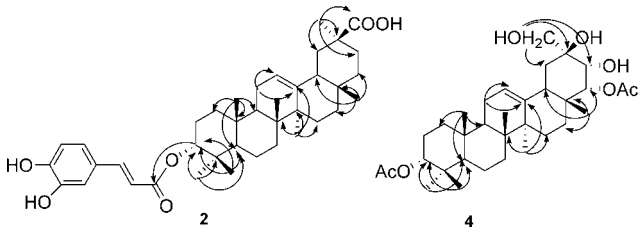

Figure 1. Selected HMBC (H→C) correlations of compounds **2** and **4**.

and 2857 cm^{-1}), conjugated-ester carbonyl (1697 cm^{-1}), and phenyl (1453, 1514, and 1603 cm^{-1}) groups. The ^1H NMR spectrum [seven tertiary methyl (δ 0.82, 0.90, 0.94, 0.98, 0.98, 1.21, and 1.24), one olefinic proton at δ 5.30 (brs), and an oxymethine proton at δ 4.78 (brs)] and the corresponding ^{13}C NMR data [seven methyls (δ 28.7, 28.2, 21.9, 15.3, 16.8, 28.0, and 26.1), a double bond (δ 122.9 and 144.0, C-12/C-13), an oxymethine (δ 78.7), and the carbonyl carbon (δ 182.7) of a carboxylic acid group] indicated that **2** was also an olean-12-enoic triterpene acid, similar to **1**. However, compound **2** differed from **1** at C-3 and C-22: the hydroxy group at C-3 in compound **1** was esterified (a comparatively low-field oxymethine proton at δ 4.78) in **2** and the hydroxy group at C-22 in **1** was absent in **2**. Furthermore, ^1H NMR data analysis showed that the hydroxy group at C-3 was esterified by caffeic acid, AM-type signals [δ 6.31 and 7.57 (d, J = 16.0 Hz)], due to the presence of protons in a *trans*-disubstituted double bond, and AMX-type signals [δ 6.88 (d, J = 8.0 Hz), 7.00 (brd, J = 8.0 Hz), and 7.13 (brs)], obtained from a 1,3,4-trisubstituted aromatic ring.[18,19] In the HMBC spectrum (Figure 1), the proton at δ 4.78 correlated with C-9′ (δ 167.5), C-23 (δ 28.2), C-24 (δ 21.9), C-4 (δ 36.8), C-2 (δ 22.8), and C-5 (δ 50.4), confirming that the caffeoyloxy group was located at C-3. Owing to the small coupling constant (brs) of H-3 with H-2, the caffeoyloxy group was assigned the 3α-orientation.[16] The correlation of H-3 with H-24 in the NOESY spectrum of **2** confirmed this conclusion. In addition, the correlations of H-22β with H-21β, H-28, and H-18 suggested that the carboxylic group was positioned at C-30. Therefore, the structure of **2** was designated as 3α-(*E*)-caffeoyloxyolean-12-en-30-oic acid.

Compound **3**, $C_{39}H_{54}O_5$ (^{13}C NMR, DEPT, and HRESIMS), showed the presence of seven tertiary methyls (δ 0.83, 0.91, 0.94, 0.98, 0.98, 1.21, and 1.23), an olefinic proton that is characteristic of H-12 [δ 5.30 (brs)] in an oleanane skeleton, an oxymethine proton [δ 4.77 (brs)], and an (*E*)-coumaroyloxy group [AM-type signals at δ 6.36 and 7.66 (d, J = 15.6 Hz) and A_2M_2-type signals at δ 6.85 and 7.46 (d, J = 8.7 Hz)] in its ^1H NMR spectrum.[20] The ^{13}C NMR spectrum (Table 1) showed 39 carbon resonances for the seven tertiary methyls (δ 15.3, 16.8, 21.9, 26.1, 28.0, 28.2, and 28.7), 10 methylenes, five methines (one olefinic, one oxygenated at δ 78.2, and three sp^3 hybridized), eight quaternary carbons (one olefinic and one carboxylic carbon at δ 182.2), and nine carbons from an (*E*)-coumaroyloxy unit. These observations showed that the structure of **3** was similar to that of **2** and that the only difference was the presence of an (*E*)-coumaroyloxy group in **3** instead of a caffeoyloxy group in **2**. The (*E*)-coumaroyloxy moiety was deduced to be present at C-3 due to the similar chemical shifts of H-3 in **3** and **2**. This was confirmed by the correlation between the proton at δ 4.77 (H-3) and the carbon at δ 167.0 (C-9′) in the HMBC spectrum of **3**. On the basis of the above evidence, compound **3** was identified as 3α-(*E*)-coumaroyloxyolean-12-en-30-oic acid.

Compound **4** showed an $[M + NH_4]^+$ peak at *m/z* 578.4050 in the HRESIMS, corresponding to a molecular formula of $C_{33}H_{52}O_7$. The IR spectrum showed the presence of hydroxy (3430 cm^{-1}) and acetoxy (1720 cm^{-1}) groups, in addition to a trisubstituted double bond (1640 cm^{-1}). The ^1H NMR spectrum displayed the characteristic signals of six tertiary methyls (δ 0.77, 0.81, 0.87, 0.92, 0.93, and 1.14), one hydroxymethyl [δ 3.14 and 3.34 (1H each, a pair of doublets, J = 11.2 Hz)], three oxymethines [δ 4.52 (brs, H-3); δ 3.56 (d, J = 3.6 Hz, H-21) and δ 4.81 (d, J = 3.6 Hz, H-22)], an olefinic [δ 5.27 (brs, H-12)], and two acetoxy methyl groups [δ 2.02 and 2.03 (s, each 3H)]. Consistent with the molecular formula empirically derived and the above ^1H NMR data, the ^{13}C NMR and DEPT spectra (Table 1) of compound **4** showed 33 carbon resonances, including six methyls (δ 25.2, 28.3, 22.3, 17.2, 15.6, and 26.1), an oxymethylene (δ 67.6, C-29), an oxygenated quaternary carbon (δ 74.2, C-20), three oxymethines (δ 77.8, C-3; 70.4, C-21; 79.3, C-22), and two acetoxy (δ 21.7, 170.6; 21.7, 170.9) groups, in addition to those of a double bond (δ 122.7 and 143.8). Accordingly, compound **4** could be designated as a normethyl oleanane-type triterpene containing a double bond and two acetoxy groups.[21–23] Comparison of the NMR spectra of **4** with those of **2** and **3** disclosed that **4** had the same A/B/C/D ring moiety as **2** and **3**, but ring E was obviously different. 2D NMR experiments were carried out to elucidate the carbon skeleton and the locations of the hydroxy, acetoxy, and normethyl groups. The cross-peaks between Me-23 (δ 0.81) and Me-24 (δ 0.87) and the carbons of an oxymethine (δ 77.8), C-4 (δ 36.7), and C-5 (δ 50.4) in the HMBC spectrum located an acetoxy group at C-3. The HMBC correlations [Me-28 (δ 0.77) to C-17 (δ 37.9), C-18 (δ 45.2), and an oxymethine (δ 79.3)] and the $^1H-^1H$ COSY correlation [the proton at δ 4.81 (1H, d, J = 3.6 Hz) with the proton at δ 3.56 (1H, d, J = 3.6 Hz)] established that the second acetoxy and a hydroxy group were in neighboring positions and linked at C-16 and C-15 or C-22 and C-21. The HMBC correlations between the proton at δ 4.81 (1H, d, J = 3.6 Hz) and the carbon of an oxymethine (δ 70.4), an oxygenated quaternary carbon (δ 74.2),

Table 1. ^{13}C NMR Data of Compounds **1**−**6** (100 MHz $CDCl_3$, δ ppm)

no.	**1**[a]	**2**	**3**	**4**[b]	**5**	**6**
1	38.7	33.9	33.8	34.0	33.7	33.7
2	26.7	22.8	22.8	22.9	22.6	22.7
3	78.5	78.7	78.2	77.8	78.2	78.2
4	38.7	36.8	36.8	36.7	36.4	36.5
5	55.5	50.4	50.3	50.4	50.0	50.0
6	18.3	18.2	18.2	18.4	18.1	18.1
7	32.6	32.6	32.5	32.8	32.5	32.5
8	39.9	40.0	39.9	40.2	39.9	40.0
9	47.8	47.6	47.5	47.7	47.3	47.3
10	36.9	36.9	36.9	37.1	36.8	36.8
11	23.4	23.4	23.4	23.6	23.4	23.4
12	122.9	122.9	122.9	122.7	123.2	123.6
13	143.8	144.0	144.1	143.8	142.7	142.2
14	42.1	41.6	41.6	42.4	42.2	42.2
15	25.6	26.1	26.1	25.9	25.6	25.5
16	19.5	27.0	27.0	23.3	23.0	22.9
17	37.5	32.0	32.0	37.9	37.7	37.8
18	48.1	48.1	48.0	45.2	44.9	44.4
19	42.4	42.7	42.7	36.3	30.9	35.3
20	43.4	44.1	44.0	74.2	78.8	73.6
21	38.6	31.1	31.1	70.4	70.0	70.8
22	76.2	38.3	38.3	79.3	78.7	78.6
23	27.5	28.2	28.2	28.3	27.7	27.8
24	14.8	21.9	21.9	22.3	21.9	21.9
25	15.1	15.3	15.3	15.6	15.3	15.3
26	16.2	16.8	16.8	17.2	16.7	16.7
27	25.4	26.1	26.1	26.1	25.7	25.7
28	24.1	28.7	28.7	25.2	24.4	24.3
29	27.9	28.0	28.0	67.6	61.5	68.6
30	179.9	182.7	182.2			
1′		127.5	127.4	CH_3CO	CH_3CO	CH_3CO
2′		115.5	129.9	21.7	21.0	21.1
3′		144.2	115.8	21.7	21.3	21.3
4′		146.5	157.5	170.6	170.2	170.5
5′		116.2	115.8	170.9	170.7	170.8
6′		122.3	129.9		OCH_3	$CH_3(CH_2)_{14}CO$
7′		144.8	144.4		48.3	14.1
8′		114.5	116.5			29.1−29.7
9′		167.5	167.0			174.7

[a] CD_3OD. [b] DMSO-d_6.

and an acetoxy carbonyl group (δ 170.6) corroborated that the acetoxy and the hydroxy groups were linked at C-22 and C-21, respectively. Furthermore, H-21 and H-22 showed correlations with C-20 (δ 74.2), whereas the two oxymethylene protons at δ 3.14/3.34 (1H each, a pair of doublets, J = 11.2 Hz) also showed correlations with C-20, which proved that CH_2OH was linked at oxygenated C-20. The stereochemistry of **4** was determined on the basis of the coupling constant [small coupling constant ($J_{21,22}$ = 3.6 Hz)] and the results of the NOE experiments. In the NOE difference spectra, irradiation of H-22 enhanced the signals of H-28 (2.80%), H-21 (2.50%), and H-18 (2.03%), which suggested that the two hydroxy groups at C-20 and C-21 and the acetoxy group at C-22 were β-, α-, and α-oriented, respectively. From the above deduction and from further comparison of the NMR data of **4** with those of known compounds,[21−24] compound **4** was identified as 3α,22α-diacetoxy-20β,21α,29-trihydroxy-30-norolean-12-ene.

From the HRESIMS data (*m/z* 592.4202 $[M + NH_4]^+$) in combination with the ^{13}C NMR and DEPT data of compound **5**, its molecular formula was proposed as $C_{34}H_{54}O_7$, 14 mass units more than compound **4**. The ^1H and ^{13}C NMR data were in good agreement with those of compound **4** except for the appearance of an additional resonance arising from a methoxy group at δ_H 3.26 (3H, s) and δ_C 48.3 (Table 1). The HMBC correlations of OCH_3/C-20; Me-28/C-21, C-17, and C-18; H-22/C-20, C-21, and the carbonyl carbon of the acetoxy group; and H-21/C-22, C-20, and C-29 showed that the hydroxy group of **4** at C-20 was displaced by a methoxy group in **5**. The configuration of **5** should be identical with that of **4**, which was confirmed by the coupling constants [the small coupling constant ($J_{21,22}$ = 3.6 Hz) and H-3 (brs)] and the NOE difference information as follows: irradiation of H-22 enhanced the signals of H-28 (2.10%), H-21 (2.70%), and H-18 (1.83%). On the basis of the above analysis, the structure of **5** was identified as 3α,22α-diacetoxy-20β-methoxy-21α, 29-dihydroxy-30-norolean-12-ene.

Compound **6** had the molecular formula $C_{49}H_{82}O_8$, as determined by HRESIMS (*m/z* 816.6348 ($[M + NH_4]^+$, calcd for 816.6348), accounting for nine degrees of unsaturation. Comparison of the ^1H and ^{13}C NMR spectra of **6** and **4** indicated that they had closely related structures, compound **6** being the 29-esterified congener of **4**. This deduction was supported by the significant downfield shift of H-29 from δ 3.14 and 3.34 (1H each, a pair of doublets, J = 11.2 Hz) of **4** to δ 3.82 (1H, d, J = 11.7 Hz) and 4.42 (1H, d, J = 11.7 Hz) of **6** and by the HMBC correlations between H-29a (δ 3.82)/H-29b (δ 4.42) and the ester carbonyl carbon (δ 174.7). Additional NMR signals corresponding to one methyl triplet at δ 0.88, one methylene triplet at δ 2.29 (α-methylene), one multiplet of 13 methylenes at δ 1.25, and a carboxylic carbon at δ 174.7 (s)[25] were observed. The ester was a palmityloxy group, which was confirmed by the HRESIMS data. The NOESY spectrum of **6** showed correlations of H-28 with H-21β and H-22β, and those of H-3 with H-24 and H-2β. From the aforementioned data, compound **6** was defined as 3α,22α-diacetoxy-29-palmityloxy-20β,21α-dihydroxy-30-norolean-12-ene.

The antimicrobial activities of compounds **1**−**6** were tested against *Staphylococcus aureus* (ATCC 25923), *Escherichia coli* (ATCC 25922), *Bacillus cereus*, and *Candida albicans.* However, none of these compounds had statistically significant antimicrobial activities (MIC > 50 μg/mL for all organisms tested).

Experimental Section

General Experimental Procedures. Optical rotations were measured using a Perkin-Elmer model 341 polarimeter. IR spectra were obtained with a Nicolet NEXUS 670 FT-IR spectrometer. NMR spectra were recorded on a Varian Mercury-400BB NMR instrument with TMS as the internal standard. HRESIMS were obtained using a Bruker APEX II mass spectrometer with glycerol as the matrix. Silica gel (200−300 mesh) was used for column chromatography and silica GF_{254} (10−40 μm) for TLC, both supplied by the Qingdao Marine Chemical Factory, Qingdao, China. TLC was detected at 254 nm or by heating after spraying with a solution of 5% H_2SO_4 in C_2H_5OH (v/v).

Plant Material. The flowers and roots of *S. muliensis* were collected from the Muli Autonomous County of Sichuan, China, in August 2005. The plant was identified by Prof. Guo-Liang Zhang from the School of Life Sciences, Lanzhou University, People's Republic of China. A voucher specimen (No. 2005004) was deposited at the Natural Product Laboratory of the College of Chemistry and Chemical Engineering, Lanzhou University, People's Republic of China.

Extraction and Isolation. The dried flowers and roots of *S. muliensis* (6.5 kg) were extracted three times (each for 7 days) with MeOH at room temperature. The filtrate was concentrated to yield a methanol extract (1800 g), which was partitioned using H_2O and petroleum ether, EtOAc, and *n*-BuOH, successively. The EtOAc extract (33 g) was subjected to column chromatography over Si gel and eluted with a gradient of petroleum ether (60−90 °C)−EtOAc (20:1, 10:1, 5:1, 2:1, 1:2, and finally MeOH). On the basis of the differences in composition indicated by TLC, six crude fractions (A−F) were collected. Fraction B was purified by repeated column chromatography on Si gel with petroleum ether (60−90 °C)−EtOAc (30:1−10:1), yielding a mixture of **7** and **8** (10 mg), and **9** (32 mg). Fraction C (5:1) was subjected to column chromatographic separation over Si gel and eluted with petroleum ether (60−90 °C)−EtOAc (8:1, 4:1, and 2:1) to yield compounds **6** (36 mg) and **11** (48 mg). Fractions D (2:1) and E (1:2) were pooled, further purified, and then subjected to column chromatography on Si gel with elution using petroleum ether (60−90 °C)−Me_2CO (5:1−1:1) to give compounds **1** (10 mg), **2** (13 mg), **3** (3 mg), **4** (8 mg), **5** (9 mg), and **10** (26 mg).

3β,22α-Dihydroxyolean-12-en-30-oic acid (1): $[\alpha]^{21}_D$ +66 (*c* 0.30, CH_3OH); IR (KBr) ν_{max} 3424, 2526, 1698 cm^{-1}; ^1H NMR (CD_3OD, 400 MHz) δ 5.27 (1H, brs, H-12), 3.36 (1H, dd, J = 12.4, 4.0 Hz, H-22), 3.15 (1H, dd, J = 10.8, 5.2 Hz, H-3), 1.18 (3H, s, H-27), 1.16 (3H, s, H-29), 1.00 (3H, s, H-26), 0.98 (3H, s, H-23), 0.97 (3H, s, H-25), 0.91 (3H, s, H-28), 0.79 (3H, s, H-24); ^{13}C NMR, see Table 1; HRESIMS *m/z* 471.3483 $[M - H]^-$ (calcd for $C_{30}H_{47}O_4$, 471.3480).

3α-(*E*)-Caffeoyloxyolean-12-en-30-oic acid (2): $[\alpha]^{21}_D$ +34 (*c* 1.00, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ϵ) 318.0, 293.6 nm; IR (KBr) ν_{max} 3389, 2930, 2857, 1697, 1690, 1603, 1514, 1453 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.57 (1H, d, J = 16.0 Hz, H-7′), 7.13 (1H, brs, H-2′), 7.00 (1H, d, J = 8.4 Hz, H-6′), 6.88 (1H, d, J = 8.0 Hz, H-5′), 6.31 (1H, d, J = 16.0 Hz, H-8′), 5.30 (1H, brs, H-12), 4.78 (1H, brs, H-3), 1.24 (3H, s, H-27), 1.21 (3H, s, H-29), 0.98 (3H, s, H-26), 0.98 (3H, s, H-25), 0.94 (3H, s, H-24), 0.90 (3H, s, H-23), 0.82 (3H, s, H-28); ^{13}C NMR, see Table 1; HRESIMS *m/z* 641.3820 $[M + Na]^+$ (calcd for $C_{39}H_{54}O_6Na$, 641.3813).

3α-(*E*)-Coumaroyloxyolean-12-en-30-oic acid (3): $[\alpha]^{21}_D$ +2.5 (*c* 0.30, $CHCl_3$); UV ($CHCl_3$) λ_{max} (log ϵ) 317.1, 293.0 nm; IR (KBr) ν_{max} 3389, 1698, 1605 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.66 (1H, d, J = 15.6 Hz, H-7′), 7.46 (2H, d, J = 8.7 Hz, H-2′and H-6′), 6.85 (2H, d, J = 8.7 Hz, H-3′ and H-5′), 6.36 (1H, d, J = 15.6 Hz, H-8′), 5.30 (1H, brs, H-12), 4.77 (1H, brs, H-3), 1.23 (3H, s, H-27), 1.21 (3H, s, H-29), 0.98 (3H, s, H-26), 0.98 (3H, s, H-25), 0.94 (3H, s, H-24), 0.91 (3H, s, H-23), 0.83 (3H, s, H-28); ^{13}C NMR, see Table 1; HRESIMS *m/z* 625.3864 $[M + Na]^+$ (calcd for $C_{39}H_{54}O_5Na$, 625.3863).

3α,22α-Diacetoxy-20β,21α,29-trihydroxy-30-norolean-12-ene (4): $[\alpha]^{21}_D$ +1.2 (*c* 0.50, CH_3OH); IR (KBr) ν_{max} 3430, 2946, 1720, 1640, 1247 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz), δ 5.27 (1H, brs, H-12), 4.81 (1H, d, J = 3.6 Hz, H-22), 4.52 (1H, brs, H-3), 3.56 (1H, d, J = 3.6 Hz, H-21), 3.34 (1H, d, J = 11.2 Hz, H-29b), 3.14 (1H, d, J = 11.2 Hz, H-29a), 2.03 (3H, s, CH_3CO), 2.02 (3H, s, CH_3CO), 1.14 (3H, s, H-27), 0.93 (3H, s, H-25), 0.92 (3H, s, H-26), 0.87 (3H, s, H-24), 0.81 (3H, s, H-23), 0.77 (3H, s, H-28); ^{13}C NMR, see Table 1; HRESIMS *m/z* 578.4050 $[M + NH_4]^+$ (calcd for $C_{33}H_{52}O_7NH_4$, 578.4051), 561.3802 $[M + H]^+$ (calcd for $C_{33}H_{53}O_7$, 561.3786), 583.3606 $[M + Na]^+$ (calcd for $C_{33}H_{52}O_7Na$, 583.3605).

3α,22α-Diacetoxy-21α,29-dihydroxy-20β-methoxy-30-norolean-12-ene (5): $[\alpha]^{21}_D$ +1.0 (*c* 0.80, $CHCl_3$); IR (KBr) ν_{max} 3423, 2945, 1720, 1646, 1247 cm^{-1}; ^1H NMR (CD_3Cl, 400 MHz) δ 5.32 (1H, brs, H-12), 4.98 (1H, d, J = 3.6 Hz, H-22), 4.64 (1H, brs, H-3), 3.91(1H, d, J = 3.6 Hz, H-21), 3.62 (2H, s, H-29), 3.26 (3H, s, OCH_3), 2.13 (3H, s, CH_3CO), 2.08 (3H, s, CH_3CO), 1.23 (3H, s, H-27), 0.97 (3H, s, H-26), 0.97 (3H, s, H-25), 0.90 (3H, s, H-28), 0.89 (3H, s, H-24), 0.86 (3H, s, H-23); ^{13}C NMR, see Table 1; HRESIMS *m/z* 592.4202 $[M + NH_4]^+$ (calcd for $C_{34}H_{54}O_7NH_4$, 592.4208), 575.3942 $[M + H]^+$

(calcd for $C_{34}H_{55}O_7$, 575.3942), 597.3753 $[M + Na]^+$ (calcd for $C_{34}H_{54}O_7Na$, 597.3762).

3α,22α-Diacetoxy-20β,21α-dihydroxy-29-palmityloxy-30-norolean-12-ene (6): $[\alpha]^{21}_D$ +2.4 (*c* 1.80, $CHCl_3$); IR (KBr) ν_{max} 3434, 2925, 2854, 1716, 1639, 1246 cm^{-1}; ^1H NMR (CD_3Cl, 400 MHz) δ 5.36 (1H, brs, H-12), 5.03 (1H, d, $J = 3.6$ Hz, H-22), 4.64 (1H, brs, H-3), 4.42 (1H, d, $J = 11.7$ Hz, H-29 b), 3.82 (1H, d, $J = 11.7$ Hz, H-29 a), 3.69 (1H, d, $J = 3.6$ Hz, H-21), 2.29 (2H, t, $J = 7.6$ Hz, H-2′), 2.13 (3H, s, CH_3CO), 2.07 (3H, s, CH_3CO), 1.22 (3H, s, H-27), 0.97 (3H, s, H-26), 0.97 (3H, s, H-25), 0.90 (3H, s, H-28), 0.90 (3H, s, H-24), 0.86 (3H, s, H-23), 0.88 (3H, t, $J = 7.5$ Hz, H-16′); ^{13}C NMR, see Table 1; HRESIMS *m/z* 816.6348 $[M + NH_4]^+$ (calcd for $C_{49}H_{82}O_8NH_4$, 816.6348), 799.6069 $[M + H]^+$ (calcd for $C_{49}H_{83}O_8$, 799.6082).

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Supporting Information Available: ^1H NMR, ^{13}C NMR, and HRESIMS of compounds **1**−**6** are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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