Six New Ursane- and Oleanane-Type Triterpenes from the Aerial Roots of *Ficus microcarpa*

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Four new ursane-type triterpenes, 3β-acetoxy-11α-methoxy-12-ursene (1), 3β-acetoxy-11α-ethoxy-12-ursene (2), 3β-acetoxy-11α-hydroperoxy-12-ursene (3), 3β-hydroxy-11α-hydroperoxy-12-ursene (4), and two new oleanane-type triterpenes, 3β-acetoxy-11α-ethoxy-12-oleanene (5), 3β-acetoxy-11α-hydroperoxy-12-oleanene (6), together with 3β-acetoxy-11α-hydroxy-12-ursene (7), 3β,11α-diacetoxy-12-ursene (8), 3β-acetoxy-11α-hydroxy-12-oleanene (9), were isolated from the aerial roots of *Ficus microcarpa* L. f. Their structures were elucidated by spectroscopic and chemical methods.

Key words *Ficus microcarpa*; 3β-acetoxy-11α-ethoxy-12-ursene; 3β-acetoxy-11α-hydroperoxy-12-ursene; 3β-hydroxy-11α-hydroperoxy-12-ursene; 3β-acetoxy-11α-ethoxy-12-oleanene; 3β-acetoxy-11α-hydroperoxy-12-oleanene

A popular ornamental *Ficus* in Taiwan is *Ficus microcarpa* L. f. (Moraceae). The chemical study of its leaves had been carried out by Higa.[1] The antiplatelet activity as well as the vigorous growth of this plant prompted us to investigate its chemical components. In previous reports, two new isoflavones together with twenty-eight other components[2] were isolated from its bark and six new compounds from its heartwood.[3] Due to our interest in this plant, we performed a chemical analysis of its aerial roots. Recently, five new taraxastane-type triterpenes have been isolated and elucidated from this part.[4] Further detailed reinvestigation of the same extract of these aerial roots has yielded six new ursane- and oleanane-type triterpenes, **1**—**6**, together with three known compounds 3β-acetoxy-11α-hydroxy-12-ursene (**7**),[5] 3β,11α-diacetoxy-12-ursene (**8**),[6] and 3β-acetoxy-11α-hydroxy-12-oleanene (**9**).[5] Four new ursene and two new oleanene derivatives were identified as 3β-acetoxy-11α-methoxy-12-ursene (**1**), 3β-acetoxy-11α-ethoxy-12-ursene (**2**), 3β-acetoxy-11α-hydroperoxy-12-ursene (**3**), 3β-hydroxy-11α-hydroperoxy-12-ursene (**4**), 3β-acetoxy-11α-ethoxy-12-oleanene (**5**), and 3β-acetoxy-11α-hydroperoxy-12-oleanene (**6**).

High resolution mass spectroscopic (HR-MS) data and ^{13}C-NMR data (Table 1) of **1** showed the formula to be $C_{33}H_{54}O_3$, indicating seven indices of hydrogen deficiency (IHD). The IR spectrum of **1** showed bands attributable to acetoxy (1737, 1244, 1082 cm^{-1}) and olefin (3050, 1670 cm^{-1}) groups. The ^{1}H-NMR spectrum of **1** exhibited signals for six singlet methyl groups (δ 0.76, 0.84, 0.84, 1.01, 1.05, 1.10), two doublet methyl groups [δ 0.84 (d, J=5.6 Hz), 0.87 (d, J=7.2 Hz)], a methine proton attached to an acetoxyl group [δ 4.48 (dd, 1H, J=7.8, 9.0 Hz)], an olefinic proton [δ 5.29 (d, 1H, J=2.8 Hz)], and an allylic proton linked to a methoxyl group [δ 3.20 (s, 3H), 3.79 (dd, 1H, J=2.8, 8.9 Hz)]. All these data suggest that compound **1** is a ursene triterpene with an acetoxyl group at C-3 and a methoxyl group at C-11. Comparision of the ^{13}C-NMR data (Table 1) of **1** with that of known 3β-acetoxy-11α-hydroxy-12-ursene (**7**)[5] suggested that **1** possesses the same skeletal structure as in **7** with a methoxyl group instead of a hydroxyl group. The methine proton at δ 3.79 (1H, dd, J=2.8, 8.9 Hz) was assigned as having a β-axial orientation at C-11 attached to a methoxyl group for the following reasons. The H-11 has a large coupling constant (J=8.9 Hz) with H-9 and is also coupled to H-12, which was proved by the decoupling method. The H-11 and a methoxyl group have a nuclear Overhauser effect (NOE) correlation and a heteronuclear multiplebond correlation (HMBC). These ^{1}H- and ^{13}C-NMR data were resolved by distortionless enhancement by polarization transfer (DEPT) and by proton-detected heteronuclear multiple-quantum coherence (HMQC) experiments. The structure was confirmed by the HMBC technique. Thus, the structure of compound **1** was deduced to be 3β-acetoxy-11α-methoxy-12-ursene.

Compound **2** has the molecular formula $C_{34}H_{56}O_3$ based on HR-MS and ^{13}C-NMR data (Table 1). The IR-spectrum showed the presence of an acetoxyl (1740, 1246, 1076 cm^{-1}) and an olefinic (3048, 1668 cm^{-1}) group. The IHD is seven, as for compound **1**. Compound **2** was deduced to be a ursene derivative due to six singlet methyl groups (δ 0.77, 0.85, 0.85, 1.00, 1.05, 1.12), two doublet methyl groups [δ 0.85 (d, J=5.2 Hz), 0.89 (d, J=7.6 Hz)], and an olefinic proton [δ 5.28 (d, J=3.2 Hz)]. It contained an acetoxyl group (δ 2.02, s) linked to C-3 [δ 4.48 (dd, 1H, J=7.6, 9.2 Hz, H-3)] and an ethoxyl group [δ 1.08 (t, 3H, J=7.2 Hz), 3.31, 3.54 (m, each 1H)] connected to C-11 [δ 3.86 (dd, 1H, J=3.2, 8.8 Hz, H-11)]. The H-11 shows a large coupling constant with H-9 and also couples to H-12. The above spectral data showed that the ethoxyl group positioned at C-11 has an α-equatorial orientation. Comparison of the ^{1}H- and ^{13}C-NMR data (Table 1) of **2** with that of **1** suggested that **2** is a derivative of ursene with an ethoxyl group instead of the methoxyl group in **1**. HMQC, HMBC, and nuclear Overhauser enhancement and exchange spectroscopy (NOESY) methods also confirmed the assigned structure. From the above evidence, compound **2** was assigned as 3β-acetoxy-11α-ethoxy-12-ursene.

The molecular formula ($C_{32}H_{52}O_4$) of compound **3**, showing one more oxygen atom than **7**, was obtained from its HR-MS and ^{13}C-NMR data (Table 1). The IR absorption bands of **3** at 3396, 3052, 1732, 1671, 1245, and 1029 cm^{-1} indicated the presence of a hydroxyl, an olefinic, and an acetoxyl groups. On account of the molecular formula of **3** being $C_{32}H_{52}O_4$, the IHD of **3** is seven, like compounds **1** and **2**. The presence of eight methyl groups could be attributed to

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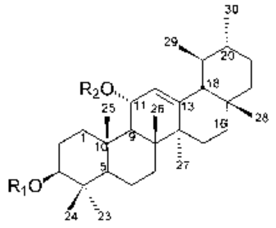
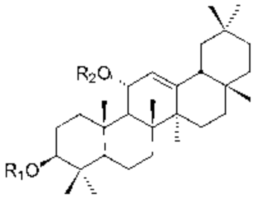
eight ^{1}H-NMR signals at δ 0.78, 0.86, 0.86, 1.05, 1.07, 1.12 (s, each 3H), 0.86 (d, 3H, J=5.2 Hz), and 0.90 (d, 3H, J=7.6 Hz). The signals at δ 2.02 (s, 3H) and 4.51 (dd, 1H, J=7.2, 8.0 Hz) were assigned as an acetoxyl group positioned at C-3. The only difference between **7** and **3** is a hydroperoxyl group present in **3** instead of the hydroxyl group in **7**. The evidence for a hydroperoxyl group is the presence of a very low field exchangeable proton at δ 7.37[7] in **3**, and signals of H-11 and C-11 positioned at a lower field [δ_H 4.52 (dd, J=3.2, 8.8 Hz) and δ_C 81.7 in **3**; δ_H 4.22 (dd, J=3.2, 8.8 Hz) and δ_C 68.3 in **7**]. Coupling constants of H-11 in **3** showed that the hydroperoxyl group had an α-equatorial orientation at C-11. Comparison of the ^{1}H- and ^{13}C-NMR data (Table 1) for **1**, **2** and **3**, showed that the structure of **3** was 3β-acetoxy-11α-hydroperoxy-12-ursene.



1 R$_1$ = Ac, R$_2$ = Me
2 R$_1$ = Ac, R$_2$ = Et
3 R$_1$ = Ac, R$_2$ = OH
4 R$_1$ = H, R$_2$ = OH
7 R$_1$ = Ac, R$_2$ = H
8 R$_1$ = R$_2$ = Ac



5 R$_1$ = Ac, R$_2$ = Et
6 R$_1$ = Ac, R$_2$ = OH
9 R$_1$ = Ac, R$_2$ = H

Compound **4** has six IHD, which was derived from its molecular formula, $C_{30}H_{50}O_3$, based on HR-MS and ^{13}C-NMR data (Table 1). The IR spectrum showed the presence of hydroxyl and olefinic groups due to absorptions at 3398, 3035, 1665 and 1040 cm^{-1}. Six singlet methyl groups, two doublet methyl groups, and an olefinic proton [δ 5.35 (d, J=3.1 Hz)] were observed in the NMR spectrum of **4**. These data indicated that it is a derivative of 12-ursene. Two oxygenated methine proton signals at δ 3.23 (dd, J=5.5, 10.7 Hz) and 4.53 (dd, J=3.1, 9.5 Hz) suggested that **4** contains one hydroxyl group at C-3 (δ_C 78.6) and one hydroperoxyl group at C-11 (δ 81.8; an exchangeable hydroxyperoxy proton at δ 7.40 was observed). Comparison of the ^{1}H- and ^{13}C-NMR data (Table 1) of **4** with those of **3**, showed that the only difference is a hydroxyl group in **4** instead of the acetoxyl group in **3**. Therefore, the structure of **4** was found to be 3β-hydroxy-11α-hydroperoxy-12-ursene.

Compound **5** was considered to be a constitutional isomer

Table 1. ^{13}C-NMR Data for **1**—**9** (100 MHz in CDCl$_3$)

Position	1	2	3	4	5	6	7	8	9
1	39.5	39.4	39.2	39.6	39.1	39.1	40.4	38.7	40.1
2	23.8	23.8	23.7	27.3	23.8	23.6	23.7	23.6	23.6
3	80.7	80.8	80.6	78.6	80.9	80.7	80.6	80.5	80.7
4	37.9	38.0$^{a)}$	38.0$^{a)}$	39.0	38.1$^{a)}$	37.7$^{a)}$	37.9	37.9$^{a)}$	37.9
5	55.3	55.3	55.2	55.1	55.4	55.1	55.3	54.9	55.3
6	18.2	18.2	18.1	18.3	18.3	18.2	18.2	18.2	18.3
7	33.5	33.4	33.3	33.4	33.4	32.9	33.5	32.8	33.1
8	42.9	42.9	43.1	43.1	43.1	43.3	43.2	43.2	43.4
9	51.8	52.0	48.8	49.1	50.9	49.5	55.7	51.9	56.3
10	37.9	37.9$^{a)}$	37.7$^{a)}$	37.8	38.0$^{a)}$	37.9$^{a)}$	37.9	37.8$^{a)}$	37.9
11	76.5	75.1	81.7	81.8	74.6	81.5	68.3	71.0	67.6
12	124.2	124.9	124.7	124.6	122.7	121.3	128.7	123.3	125.4
13	143.6	143.0	146.1	146.2	149.0	152.8	142.9	145.5	149.3
14	42.0	42.0	42.0	42.0	41.7	41.7	42.1	41.8	41.8
15	26.7	26.7	26.7	26.8	26.3	26.3	26.6	26.8	26.2
16	27.9	27.9	27.8	27.8	26.8	26.7	27.9	27.8	26.7
17	33.6	33.6	33.6	33.6	32.3	32.2	33.6	33.4	32.3
18	58.5	58.5	58.4	58.4	47.0	46.8	58.1	57.7	46.5
19	39.3$^{b)}$	39.4$^{b)}$	39.3$^{b)}$	39.3$^{b)}$	46.5	46.7	39.2$^{b)}$	39.4	46.5
20	39.5$^{b)}$	39.5$^{b)}$	39.4$^{b)}$	39.4$^{b)}$	31.1	31.1	39.4$^{b)}$	39.4	31.1
21	31.1	31.1	31.1	31.1	34.7	34.6	31.0	31.1	34.6
22	41.4	41.4	41.3	41.3	37.0	36.9	41.3	41.2	36.9
23	28.2	28.2	28.2	28.2	28.2	28.1	28.2	28.0	28.1
24	16.7	16.7	16.7	15.6	16.7	16.6	16.8	16.5	16.6
25	16.9	17.0	16.7	16.7	16.8	16.9	16.8	16.9	16.9
26	18.2	18.2	18.1	18.1	18.2	18.2	17.9	18.0	18.3
27	22.5	22.5	22.0	22.0	25.1	24.7	23.1	22.4	26.2
28	28.7	28.7	28.6	28.6	28.5	28.5	28.6	28.7	28.4
29	17.4	17.4	17.5	17.5	33.3	33.3	17.6	17.3	33.2
30	21.3	21.3	21.3	21.3	23.7	23.6	21.3	21.3	23.6
$3\text{-CH}_3\underline{\text{C}}\text{O}$	170.8	170.9	171.0		171.0	171.0	171.0	171.0	170.9
$3\text{-}\underline{\text{C}}\text{H}_3\text{CO}$	21.3	21.3	21.3		21.3	21.3	21.3	21.4	21.3
OCH_3	54.2								
$\text{CH}_3\underline{\text{C}}\text{H}_2\text{O}$		62.0			60.8				
$\underline{\text{C}}\text{H}_3\text{CH}_2\text{O}$		15.9			15.9				
$11\text{-CH}_3\underline{\text{C}}\text{O}$								171.2	
$11\text{-}\underline{\text{C}}\text{H}_3\text{CO}$								21.7	

a, *b*) Values bearing the same superscript may be interchanged.

of **2** on the basis of HR-MS and ^{13}C-NMR data (Table 1), together with the fact that the molecular formula, $C_{34}H_{56}O_3$, had seven IHD. Its IR spectrum showed the presence of an acetoxyl and an olefinic group (3040, 1736, 1670, 1245, and 1077 cm^{-1}). Compound **5** is a 12-oleanene derivative with eight singlet methyl groups [δ 0.81, 0.86, 0.86, 0.87, 0.87, 0.98, 1.05, 1.19 (s, each 3H)] and an olefinic proton [δ 5.26 (d, J=3.3 Hz)]. An acetoxyl group connected to C-3 caused the H-3 signal downfield at δ 4.49 (dd, J=7.0, 9.3 Hz). The signals at δ 3.28, 3.50 (m, each 1H), and 1.10 (t, 3H, J=7.2 Hz) was due to an ethoxyl group which is located at C-11, suggesting H-11 at δ 3.97 (dd, J=3.3, 9.1 Hz). The chemical shift and coupling pattern of the H-3 and H-11 of **5** are similar to those of **2**. Comparison of the ^{1}H- and ^{13}C-NMR data of **5** with that of **9** suggested that the only difference is an ethoxyl group in **5** instead of the hydroxy group in **9**. This evidence showed that the structure of **5** is 3β-acetoxy-11α-ethoxy-12-oleanene. HMBC and NOESY techniques also confirmed the assigned structure.

Compound **6** is a constitutional isomer of **3** based on its molecular formula of $C_{32}H_{52}O_4$ which was determined from HR-MS and ^{13}C-NMR data (Table 1). Eight singlet methyl groups [δ 0.82, 0.86, 0.86, 0.86, 0.87, 0.99, 1.04, 1.20 (s, each 3H)] and an olefinic proton [δ 5.42 (d, J=3.6 Hz)] confirmed that **6** is an oleanene derivative. Its IR spectrum contained hydroxyl (3406 cm^{-1}), acetoxyl (1734, 1268, 1030 cm^{-1}), and olefinic (3045, 1667 cm^{-1}) groups. Its ^{1}H-NMR data were similar to those of compound **5** except for the presence of a hydroperoxy group (δ 7.51, s, exchangeable with D_2O) instead of the ethoxyl group in **5**. The H-11 exhibited a downfield shift at δ 4.47 (dd, J=3.6, 8.8 Hz) compared with the corresponding proton in **9** [δ 4.16 (dd, J=3.6, 8.0 Hz)] or in **5** [δ 3.97 (dd, J=3.3, 9.1 Hz)]. Comparison of the ^{1}H- and ^{13}C-NMR spectra data (Table 1) of **6** with that of **5** indicated that **6** is 3β-acetoxy-11β-hydroperoxy-12-oleanene.

The chemical correlation of the six new ursene and oleanene derivatives listed above was carried out as follows. Compound **1** can be prepared from **7** in diluted methanolic HCl solution. Treatment of **7** and **9** with dilute HCl in ethanol yielded **2** and **5**, respectively. The exchange of the hydroxyl group for an alkoxyl group was an *S*N1 reaction, and the alkoxyl group attacked from the less hindered α-face. Triphenyl phosphine reduction of **3** and **6** affored **7** and **9**, respectively. The ^{13}C-NMR data of compounds **7**, **8**, and **9** have not been reported in the literature, and therefore, they are given in Table 1 for comparison.

Experimental

Melting points were determined with a Yanagimoto micromelting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 983G spectrophotometer. ^{1}H- and ^{13}C-spectra were recorded on a Varian Unity Plus 400 spectrometer and a Bruker AM-300 spectrometer. EI-MS and specific rotations were recorded on a JEOL JMS-HX 300 mass spectrometer and a JASCO DIP-1000 digital polarimeter, respectively. Extracts were chromatographed on silica gel (Merck 70—230, 230—400 mesh, ASTM).

Extraction and Isolation The dried aerial roots of *Ficus microcarpa* L. f. were crushed to give 18 kg of raw material, which was extracted with MeOH (150 l) at room temperature (7 d×2). The extract was evaporated *in vacuo* to yield a residue which was suspended in H_2O (1 l), and this phase was then partitioned with ethyl acetate (1 l×3). The combined ethyl acetate layers afforded a black syrup (250 g) which was subsequently chromatographed on silica gel using a hexane/EtOAc gradient solvent system. Crude compounds, **1**—**9**, were all eluted with 20% EtOAc in hexane. Further purification by HPLC [Merck LichroCART 250-10 Cat. 1.50179 Lichrosorb Si 60 (7 μm)] gave **1** (47 mg), **2** (25 mg), **5** (6 mg), **8** (5 mg), **3** (225 mg), **6** (5 mg), **7** (50 mg), **9** (6 mg) and **4** (21 mg) using 5% EtOAc/hexane, 5% EtOAc/hexane, 5% EtOAc/hexane, 10% EtOAc/hexane, 15% EtOAc/hexane, 15% EtOAc/hexane, 20% EtOAc/hexane, 20% EtOAc/hexane, and 30% EtOAc/hexane, respectively. Three known compounds, **7**, **8** and **9**, were identified by comparing their physical data with that in the literature.

3β-Acetoxy-11α-methoxy-12-ursene (**1**): mp 129—131 °C, $[\alpha]_D^{26}$ +6.7° (c=4.7, CHCl$_3$). IR ν_{max} cm^{-1}: 3050, 1737, 1670, 1378, 1368, 1244, 1082, 1029. ^{1}H-NMR (300 MHz, CDCl$_3$) δ: 0.76, 0.84, 0.84, 1.01, 1.05, 1.10, 2.00, 3.20 (s, each 3H), 0.84 (d, 3H, J=5.6 Hz), 0.87 (d, 3H, J=7.2 Hz), 3.79 (dd, 1H, J=2.8, 8.9 Hz, H-11), 4.48 (dd, 1H, J=7.8, 9.0 Hz, H-3), 5.29 (d, 1H, J=2.8 Hz, H-12). ^{13}C-NMR data see Table 1. EI-MS (70 eV) m/z (rel. int. %): 498 (M$^+$, 17), 467 (37), 466 (100), 406 (85), 391 (38), 255 (41). HR-EI-MS m/z M$^+$ Calcd for $C_{33}H_{54}O_3$: 498.4075. Found 498.4073.

3β-Acetoxy-11α-ethoxy-12-ursene (**2**): mp 151—155 °C, $[\alpha]_D^{25}$ +11.0° (c=2.5, CHCl$_3$). IR ν_{max} cm^{-1}: 3048, 1740, 1668, 1382, 1369, 1246, 1076, 1030, 986. ^{1}H-NMR (400 MHz, CDCl$_3$) δ: 0.77, 0.85, 0.85, 1.00, 1.05, 1.12, 2.02 (s, each 3H), 0.85 (d, 3H, J=5.2 Hz), 0.89 (d, 3H, J=7.6 Hz), 1.08 (t, 3H, J=7.2 Hz), 1.68 (d, 1H, J=8.8 Hz, H-9), 3.31, 3.54 (m, each 1H, –OC$\underline{H}_2$CH$_3$), 3.86 (dd, 1H, J=3.2, 8.8 Hz, H-11), 4.48 (dd, 1H, J=7.6, 9.2 Hz, H-3), 5.28 (d, 1H, J=3.2 Hz, H-12). ^{13}C-NMR data see Table 1. EI-MS (70 eV) m/z (rel. int. %): 512 (M$^+$, 42), 467 (36), 466 (87), 406 (30), 391 (22), 279 (64), 167 (100). HR-EI-MS m/z M$^+$ Calcd for $C_{34}H_{56}O_3$: 512.4231. Found 512.4216.

3β-Acetoxy-11α-hydroperoxy-12-ursene (**3**): mp 184—186 °C, $[\alpha]_D^{31}$ +14.3° (c=2.6, CHCl$_3$). IR ν_{max} cm^{-1}: 3396, 3052, 1732, 1671, 1380, 1368, 1245, 1029, 983. ^{1}H-NMR (400 MHz, CDCl$_3$) δ: 0.78, 0.86, 0.86, 1.05, 1.07, 1.12, 2.02 (s, each 3H), 0.86 (d, 3H, J=5.2 Hz), 0.90 (d, 3H, J=7.6 Hz), 1.73 (dt, 1H, J=5.6, 13.6 Hz, H$_\beta$-15), 1.87 (d, 1H, J=8.8 Hz, H-9), 2.01 (dt, 1H, J=4.8, 13.6 Hz, H$_\alpha$-16), 2.14 (td, 1H, J=3.6, 13.6 Hz, H$_\beta$-1), 4.51 (dd, 1H, J=7.2, 8.0 Hz, H-3), 4.52 (dd, 1H, J=3.2, 8.8 Hz, H-11), 5.33 (d, 1H, J=3.2 Hz, H-12), 7.37 (s, 1H, –OOH, exchangeable with D_2O). ^{13}C-NMR data see Table 1. EI-MS (70 eV) m/z (rel. int. %): 500 (M$^+$, 1), 482 (M$^+$−H$_2$O, 17), 467 (44), 466 (100), 406 (24), 273 (45), 232 (31). HR-EI-MS m/z M$^+$ Calcd for $C_{32}H_{52}O_4$: 500.3867. Found 500.3871.

3β-Hydroxy-11α-hydroperoxy-12-ursene (**4**): mp 95—97 °C, $[\alpha]_D^{25}$ +29.1° (c=2.1, CHCl$_3$). IR ν_{max} cm^{-1}: 3398, 3035, 1665, 1381, 1040. ^{1}H-NMR (300 MHz, CDCl$_3$) δ: 0.79, 0.79, 0.99, 1.05, 1.05, 1.13 (s, each 3H), 0.87 (d, 3H, J=5.9 Hz), 0.91 (d, 3H, J=6.6 Hz), 1.83 (d, 1H, J=9.5 Hz, H-9), 2.01 (dt, 1H, J=4.3, 13.1 Hz, H$_\alpha$-16), 2.12 (td, 1H, J=3.4, 13.5 Hz, H$_\beta$-1), 3.23 (dd, 1H, J=5.5, 10.7 Hz, H-3), 4.53 (dd, 1H, J=3.1, 9.5 Hz, H-11), 5.35 (d, 1H, J=3.1 Hz, H-12), 7.40 (s, 1H, –OOH, exchangeable with D_2O). ^{13}C-NMR data see Table 1. EI-MS (70 eV) m/z (rel. int. %): 458 (M$^+$, 1), 440 (M$^+$−H$_2$O, 4), 424 (35), 273 (28), 113 (45), 119 (74), 105 (100), 91 (90). HR-EI-MS m/z M$^+$ Calcd for $C_{30}H_{50}O_3$: 458.3762; Found 458.3747.

3β-Acetoxy-11α-ethoxy-12-oleanene (**5**): mp 195—198 °C, $[\alpha]_D^{32}$ +22.4° (c=0.2, CHCl$_3$). IR ν_{max} cm^{-1}: 3040, 1736, 1670, 1383, 1364, 1245, 1077, 1028, 984. ^{1}H-NMR (300 MHz, CDCl$_3$) δ: 0.81, 0.86, 0.86, 0.87, 0.87, 0.98, 1.05, 1.19, 2.03 (s, each 3H), 1.10 (t, 3H, J=7.2 Hz, –OCH$_2$CH$_3$), 1.75 (d, 1H, J=9.1 Hz, H-9), 3.28, 3.50 (m, each 1H, –OCH$_2$CH$_3$), 3.97 (dd, 1H, J=3.3, 9.1 Hz, H-11), 4.49 (dd, 1H, J=7.0, 9.3 Hz, H-3), 5.26 (d, 1H, J=3.3 Hz, H-12). ^{13}C-NMR data see Table 1. EI-MS (70 eV) m/z (rel. int. %): 512 (M$^+$, 14), 467 (22), 466 (65), 406 (100), 391 (61), 255(48). HR-EI-MS m/z M$^+$ Calcd for $C_{34}H_{56}O_3$: 512.4231. Found 512.4225.

3β-Acetoxy-11α-hydroperoxy-12-oleanene (**6**): Amorphous, $[\alpha]_D^{29}$ +2.5° (c=0.5, CHCl$_3$). IR ν_{max} cm^{-1}: 3406, 3045, 1734, 1667, 1385, 1268, 1249, 1030, 984. ^{1}H-NMR (400 MHz, CDCl$_3$) δ: 0.82, 0.86, 0.86, 0.86, 0.87, 0.99, 1.04, 1.20, 2.03 (s, each 3H), 1.87 (d, 1H, J=8.8 Hz, H-9), 4.47 (dd, 1H, J=3.6, 8.8 Hz, H-11), 4.50 (dd, 1H, J=5.6, 10.4 Hz, H-3), 5.42 (d, 1H, J=3.6 Hz, H-12), 7.51 (s, 1H, –OOH, exchangeable with D_2O). ^{13}C-NMR data see Table 1. EI-MS (70 eV) m/z (rel. int. %): 500 (M$^+$, 1), 482 (M$^+$−H$_2$O, 10), 467 (45), 466 (100), 407 (25), 406 (24), 273 (23), 255 (40), 232 (42), 84 (92). HR-EI-MS m/z M$^+$ Calcd for $C_{32}H_{52}O_4$: 500.3867. Found 500.3842.

Treatment of 7 with HCl in MeOH Compound **7** (9.5 mg) and one drop of conc. HCl were added to MeOH (3 ml). The mixture was stirred at room temperature for 15 min, and at the end of the reaction, 0.5 ml of 1 N aqueous NaHCO$_3$ was added. After the usual treatment, the product was identified as compound **1** (8.0 mg).

Treatment of 7 or 9 with HCl in EtOH Compound **7** (8.4 mg) and one drop of conc. HCl were added to EtOH (3 ml) and left for 15 min at room temperature. The product was identified as compound **2** (8.0 mg) using the method described above. Following similar treatment, compound **9** afforded compound **5** in good yield.

Reduction of 3 (or 6) with Triphenyl Phosphine Compound **3** (7 mg) and Ph_3P (4 mg) were dissolved in $CHCl_3$ (1 ml) over 20 min with stirring. After the usual purification, compound **7** was obtained in quantitative yield. Compound **9** was prepared in quantitative yield from compound **6** by a similar reduction.

Acknowledgments This research was supported by the National Science Council of the Republic of China.

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