Triterpenoids and Aromatics from *Derris laxiflora*

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Seven new compounds, *O-trans*-cinnamoylglutinol (**1**), 22β-hydroxy-12-oleanen-3-one (**2**), 15α,16α-epoxy-12-oleanen-3-one (**3**), 29-hydroxy-12-oleanene-3,22-dione (**4**), 22β,29-dihyroxy-12-oleanen-3-one (**5**), 2,3-(methylenedioxy)-4-methoxy-5-methylphenol (**8**), and 2,3,6-trimethoxy-5-methylphenol (**9**), as well as two first isolated from natural sources, 25-cycloartene-3,24-dione (**6**) and 24ξ-hydroxy-25-cycloarten-3-one (**7**), were characterized from *Derris laxiflora*. The structures of these compounds were determined by analysis of their spectroscopic data.

Derris laxiflora Benth. (Leguminosae) is a native species found on the hills and lowlands of southern Taiwan, and its extract is used traditionally as an insecticide and piscicide.[1] Seven flavonoids, including 3′-methoxylupinifonin, laxifolin, isolaxifolin, laxichalcone, derrichalcone, derriflavanone, and *epi*-derriflavanone, have been isolated and identified from ethanolic extract of the roots.[1,2] However, to the best of our knowledge there is no prior report on the constituents from whole plants of *D. laxiflora*. In this study, we describe the isolation and structural elucidation of five new triterpenoids (**1**−**5**), 25-cycloartene-3,24-dione (**6**),[3] 24ξ-hydroxy-25-cycloarten-3-one (**7**),[4]and two new aromatics (**8**, **9**) from *D. laxiflora*.

Results and Discussion

The molecular formula of compound **1** was assigned as $C_{39}H_{56}O_2$ (M^+; *m*/*z* 556.4271) by HREIMS. The IR spectrum suggested that it contained an ester (1709 cm^{-1}) and a conjugated double bond (1645 cm^{-1}). The ^1H NMR spectrum (see Experimental Section) showed eight methyl groups (each 3H, s), a trisubstituted olefinic proton [δ_H 5.58 (br d), J = 5.6 Hz] characteristic of H-6 of the glutinane skeleton,[5] a proton signal characteristic of H-3 [δ_H 4.82 (1H, br t), J = 2.4 Hz], and a (*E*)-cinnamoyl group [δ_H 6.38 and 7.61 (1H each, d, J = 16.0 Hz), δ_H 7.36 (3H, m), δ_H 7.48 (2H, m)] attached to a tertiary carbon. The ^{13}C NMR spectrum of **1** (Table 1) was similar to those of glutinol, except that **1** showed additional signals of an (*E*)-cinnamoyl moiety [δ_C 166.5 (C-1′), 118.9 (C-2′), 144.2 (C-3′), 134.6 (C-4′), 128.0 (C-5′, C-9′), 128.8 (C-6′), 130.1 (C-7′, C-8′)]. The HMBC spectrum of **1** showed a long-range correlation between H-3 (δ_H 4.82) and C-1′ (δ_C 166.5), and several key NOESY correlations (H_3-24/H-3, H-6; H_3-23/H-10) suggested that the *O-trans*-cinnamoyl group was attached to C-3 with β-axial orientation (Figure 1). Hence, compound **1** was established as *O-trans*-cinnamoylglutinol.

Compound **2** was assigned as $C_{30}H_{48}O_2$ (M^+; *m*/*z* 440.3650) by HREIMS. The IR spectrum showed the presence of OH (3476 cm^{-1}) and carbonyl groups (1699 cm^{-1}). The ^1H NMR spectrum showed eight methyl signals (each 3H, s), an olefinic proton characteristic of H-12 [δ_H 5.26 (1H, t, J = 3.6 Hz)] of an oleanene skeleton,[6] and an oxymethine proton [δ_H 3.43 (1H, t, J = 5.2 Hz, H-22)]. The ^{13}C NMR spectrum of **2** (Table 1) showed a signal of a ketone group (δ_C 217.8) and two olefinic carbon signals (δ_C 122.6, 143.9), which were in good agreement with those of C-12 and C-13 of olean-12-ene derivatives.[7] The HMBC spectrum of **2** showed long-range correlations from H_3-24 (δ_H 1.04) and H_3-23 (δ_H 1.08) to C-3, C-4, and C-5; between H-12 (δ_H 5.26) and C-9, C-14, and C-18; and between H_3-28 (δ_H 0.86) and C-16, C-18, and C-22. In addition, significant NOEs were observed between H-18 and H-12, H_3-28, and H_3-30; and between H-22 and H_2-21. Accordingly, the

Table 1. ^{13}C NMR Chemical Shifts (δ) of Compounds **1**−**5** (125 MHz, $CDCl_3$)

carbon	**1**	**2**	**3**	**4**	**5**
1	19.9	39.3	38.4	39.3	39.6
2	25.5	34.2	27.1	34.1	34.2
3	78.6	217.8	78.9	217.6	217.9
4	39.3	47.4	38.7	48.0	47.4
5	142.0	55.3	55.1	55.3	55.2
6	120.1	19.6	18.3	19.6	19.6
7	23.5	32.4	32.3	32.2	32.3
8	47.4	39.6	39.1	39.6	39.6
9	34.9	46.9	47.5	46.8	46.8
10	49.8	36.7	37.2	36.6	36.6
11	35.1	23.6	23.3	23.6	23.6
12	30.4	122.6	122.6	123.8	122.6
13	37.9	143.9	140.4	141.5	143.7
14	39.3	42.2	41.6	42.0	42.4
15	32.0	25.8	55.6	25.1	25.8
16	38.9	28.2	64.8	26.8	28.2
17	30.1	37.4	32.5	47.4	37.8
18	43.1	44.9	48.5	47.0	44.0
19	33.1	46.1	44.7	40.6	40.3
20	28.2	30.5	30.4	39.0	35.6
21	34.5	41.5	35.6	45.6	36.0
22	36.0	76.6	35.6	217.0	76.2
23	29.0	26.5	28.0	26.5	26.5
24	25.2	21.5	15.5	21.5	21.5
25	16.1	15.3	15.4	15.3	15.3
26	19.5	16.9	18.7	16.7	16.9
27	18.4	25.3	22.9	25.3	25.3
28	32.0	20.0	26.3	20.7	19.9
29	34.5	32.7	33.0	72.5	73.2
30	32.4	28.2	23.7	21.0	23.3
1′	166.5				
2′	118.9				
3′	144.2				
4′	134.6				
5′, 9′	128.0				
6′, 8′	128.8				
7′	130.1				

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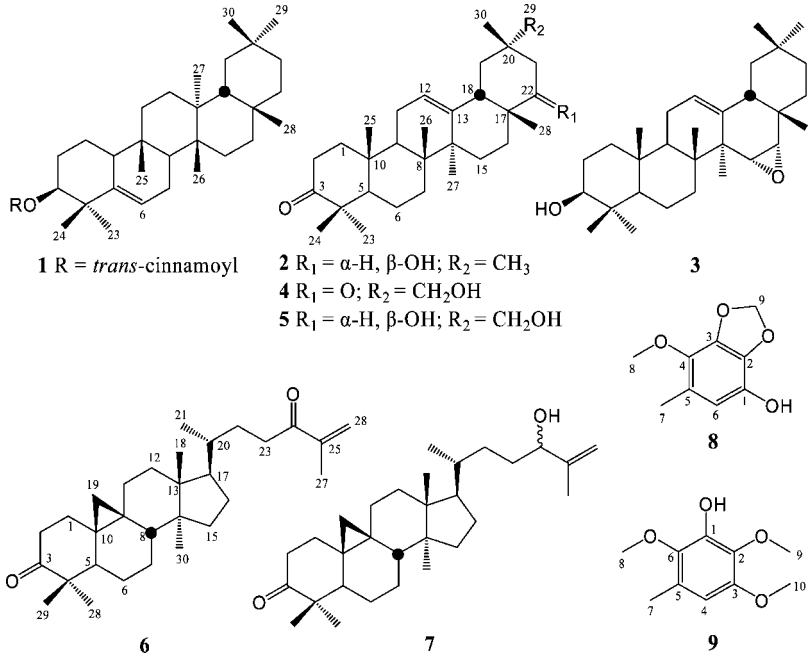

secondary OH group was assigned as C-22 axial, and it caused the H-18 signal to shift downfield to δ 2.09. The coupling constant of H-22 indicates that it is equatorial in orientation. Hence, compound **2** was established as 22β-hydroxyl-12-oleanen-3-one.

Compound **3** was assigned the molecular formula $C_{30}H_{48}O_2$ (M^+; *m/z* 440.3649) by HREIMS. The IR spectrum showed the presence of an OH group (3423 cm^{-1}). Eight ^1H NMR signals (each 3H, s) were attributed to methyl groups. Comparison of ^1H and ^{13}C NMR data of **3** with those of **2** suggested that **3** was an oleanane derivative. The ^{13}C NMR signal at δ_C 78.9 and corresponding proton signal at δ_H 3.21 (1H, dd, J = 11.6, 4.5 Hz) were assigned as C-3 and H-3α, respectively. In addition, two olefinic carbon signals (δ_C 122.6, 140.4) were observed, and the calculated number of rings for **3** was seven, including a pentacyclic skeleton. Accordingly, the remaining two oxygenated carbons at δ_C 55.6 [corresponding proton signal at δ_H 2.89 (1H, d, J = 3.5 Hz)] and δ_C 64.8 [corresponding proton signal at δ_H 2.77 (1H, d, J = 3.5 Hz)] were assigned to an epoxide functionality. NOESY correlations of H_3-28/H-16 and H_3-26/H-15 indicated that both H-15 and H-16 were β-oriented, and HMBC supported the assigned structure. Thus, compound **3** was established as 15α,16α-epoxy-12-oleanen-3β-ol.

Compounds **4** and **5** were assigned the molecular formula $C_{30}H_{46}O_3$ and $C_{30}H_{48}O_3$, respectively, by HREIMS. The IR spectra of both compounds showed the presence of OH ($\sim$3400 cm^{-1}) and carbonyl groups (1699 cm^{-1}). The ^1H and ^{13}C NMR data of **5** closely resembled those of **2**, except for the presence of an oxymethylene group [δ_H 3.25 (2H, s); δ_C 73.2] instead of a tertiary methyl group in **2**. The HMBC correlations of H_2-29 (δ_H 3.25) and H_3-30 (δ_H 3.25) to C-19, C-20, and C-21 revealed that the oxymethylene and methyl groups were attached to C-20. In addition,

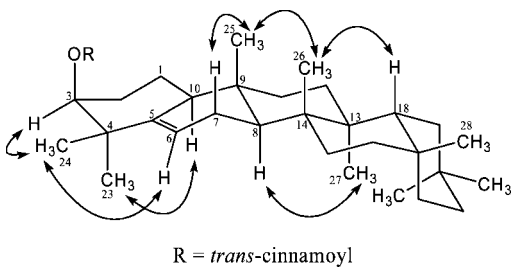

Figure 1. Key NOESY correlations of *O-trans*-cinnamoylglutinol (**1**).

NOE correlation of H_3-30 to H-18 indicated that the H_3-30 was β-oriented. Hence, compound **5** was established as 22β,29-dihydroxyl-12-oleanen-3-one. As to the structure of **4**, its IR and NMR data were similar to those of **5**, except for the C-22 substituent. In the HMBC spectrum, correlations of H_3-28 (δ_H 1.01) and H_2-21 (δ_H 2.00, 2.58) to δ_C 217.0 indicated that the carbonyl group was attached to C-22. Thus, compound **4** was identified as 29-hydroxy-12-oleanene-3,22-dione.

The molecular formula of **6**, $C_{30}H_{46}O_2$, was established from HREIMS and ^{13}C NMR data. Its IR spectrum indicated the presence of isolated and conjugated ketone groups (1709, 1678 cm^{-1}). ^1H NMR data showed five methyl singlets (δ_H 0.88, 0.97, 1.02, 1.08, 1.85), a secondary methyl group at δ_H 0.87 (3H, d, J = 5.6 Hz), terminal methylene protons at δ_H 5.94 (1H, br s) and 5.73 (1H, br s), and two doublet protons for a cyclopropyl CH_2 group at δ_H 0.55 (1H, d, J = 4.3 Hz) and 0.76 (1H, d, J = 4.3 Hz), indicating a cycloartane skeleton. The mass spectrum showed fragment ions at *m/z* 313 [M $-$ $C_8H_{13}O$ (side chain)]$^+$ and 175 [M $-$ $C_{17}H_{27}O_2$ (side chain + ring A)]$^+$. The HMBC spectrum of **6** showed long-range correlations from H_2-22, H_2-26, and H_3-27 to C-24; from H_3-21 to C-17 and C-22; and between H_3-18 and C-17. These results suggested that **6** possessed a C_8-side-chain with a conjugated carbonyl group [UV (MeOH) λ_{max} 224 and 261 nm] on the five-membered ring. On the other hand, in the HMBC spectrum, the signals of H_3-28 and H_3-29 correlated with that of the oxo group (δ_C 216.6), indicating that the oxo group was located at C-3 and which caused the H_2-19 signals of the cyclopropane ring to appear downfield to δ_H 0.76 (d, J = 4.3 Hz, H_{endo}) and 0.55 (d, J = 4.3 Hz, H_{exo}), respectively.[8] Thus, compound **6** was identified as 25-cycloartene-3,24-dione. This is the first report of **6** from a natural source; however, Djerassi and McCrindle had prepared this compound from 3β-hydroxy-24-cycloartene with chromic acid in acetone.[3]

Compound **7** had the molecular formula $C_{30}H_{48}O_2$ based on HREIMS and ^{13}C NMR data. Its IR spectrum indicated the presence of OH (3423 cm^{-1}) and oxo (1706 cm^{-1}) groups. ^1H NMR data of **7** were similar to those of **6**, except for the presence of an OH group [δ_H 4.00 (1H, t, J = 6.6 Hz)] instead of an oxo group. This oxymethine proton was assigned at C-24 due to its chemical shift and coupling pattern as well as HMBC correlation to C-25, -26, and -27. ^1H and ^{13}C data suggested that **7** was 24ξ-hydroxy-25-cycloarten-3-one, not previously isolated from natural sources,

Table 2. ^{1}H (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$) Chemical Shifts (δ) of Compounds **8** and **9**

	8		**9**	
position	δ_C	δ_H	δ_C	δ_H
1	134.3		142.5	
2	133.3		134.5	
3	138.4		148.5	
4	135.7		104.4	6.22 s
5	124.0		125.7	
6	111.6	6.23 s	139.8	
7	15.5	2.09 s	15.8	2.21 s
8	59.9	3.84 s	60.5	3.76 s
9	101.3	5.85 s	61.0	3.86 s
10			56.0	3.79 s

though it had been prepared from cycloartenone by biotransformation using the fungus *Glomerella fusarioides*.[4]

The molecular formula of **8**, $C_9H_{10}O_4$, was established from HREIMS and ^{13}C NMR data. The IR spectrum suggested that **8** was a benzenoid (1626, 1510, and 1471 cm^{-1}) bearing a hydroxyl (3441 cm^{-1}) functionality. The ^{1}H NMR spectrum (Table 2) showed signals for one methyl group [δ_H 2.09 (3H, s, H_3-7)], one methoxy group [δ_H 3.84 (3H, s, H_3-8)], one methylenedioxy group [δ_H 5.85 (2H, s, H_2-9)], and a single aromatic proton resonance [δ_H 6.23 (1H, s, H-6)]. The HMBC spectrum of **8** revealed that the methylenedioxy proton signal H_2-9 (δ_H 5.85, s) coupled to C-2 (δ_C 133.3) and C-3 (δ_C 138.4), the H-6 signal (δ_H 6.23) coupled to C-1 (δ_C 134.3), C-2 (δ_C 133.3), C-4 (δ_C 135.7), and C-5 (δ_C 124.0), the H_3-8 signal (δ_H 3.84) coupled to C-4 (δ_C 135.7), and the H_3-7 signal (δ_H 2.09) coupled to C-4 (δ_C 135.7), C-5 (δ_C 124.0), and C-6 (δ_C 111.6). In combination with the HMBC assignments, mutual correlations including H-6/H_3-7 and H_3-7/H_3-8 in the NOESY spectrum helped to confirm both δ_C 111.6/δ_C 138.4 and δ_C 124.0/δ_C 133.3 should be *para*-oriented. The locations of all functionalities borne by the benzene ring were thus determined. Accordingly, compound **8** was identified as 2,3-(methylenedioxy)-4-methoxy-5-methylphenol.

Compound **9** was assigned as $C_{10}H_{14}O_4$ (M^+; *m*/*z* 198.0885) by HREIMS. Analysis of the IR spectrum of **9** suggested that it contained a hydroxyl group (3421 cm^{-1}) and a benzene ring (1605, 1508 cm^{-1}). The ^{1}H NMR spectrum (Table 2) showed that **9** has a methyl group [δ_H 2.21 (3H, s, H_3-7)] and three methoxyl groups [δ_H 3.76 (3H, s, H_3-8), 3.86 (3H, s, H_3-9), and 3.79 (3H, s, H_3-10)] attached to an aromatic functionality, and a single proton signal at δ_H 6.22 (1H, s, H-4). Heteronuclear long-range correlations [δ_H 6.22 (H-4) coupled to δ_C 134.5 (C-2), 148.5 (C-3), 125.7 (C-5), 139.8 (C-6); δ_H 2.21 (H_3-7) coupled to δ_C 125.7 (C-5), 104.4 (C-4), 139.8 (C-6); δ_H 3.76 (H_3-8) coupled to C-6, δ_H 3.86 (H_3-9) coupled to C-2; δ_H 3.79 (H_3-10) coupled to C-3] in combination with the NOESY techniques (H-4/H_3-7, H_3-10; H_3-7/H_3-8) corroborated the locations of four functional groups on the benzene ring. The remaining hydroxyl group must be located at C-1, as evidenced from the analysis of above spectral interpretations. Conclusively, compound **9** was established as 2,3,6-trimethoxy-5-methylphenol.

Experimental Section

General Experimental Procedures. Melting points were determined on a Yanaco MP-S3 micromelting point apparatus without correction. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter in MeOH at 25 °C. UV spectra were taken on a Hitachi UV-3210 spectrophotometer. IR spectra were recorded on a Nicolet Magna-IR 550 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 spectrometer, and the solvent resonance was used as internal shift reference. EIMS and HREIMS were determined on a Finnigan TSQ-46C and JEOL SX-102A mass spectrometers. Column chromatography was carried out with silica gel (70−230 and 230−400 mesh, Merck 7734). HPLC was run on a GBC LC-1440 instrument equipped with a refractive index (RI) detector.

Plant Material. The whole plant of *D. laxiflora* was collected in Taitong County, Taiwan, in December 2001. The plant material was identified by Prof. Shang-Tzen Chang of School of Forestry and Resource Conservation, National Taiwan University, and a voucher specimen was deposited at the herbarium of School of Forestry and Resource Conservation, National Taiwan University, Taipei, Taiwan.

Extraction and Isolation. Air-dried pieces of the whole plant of *D. laxiflora* (11.7 kg) were extracted with MeOH (140 L) by soaking for 1 week each at room temperature two times. The extract was filtered under vacuum and concentrated in a rotary evaporator to a residue (400 g). The residue was suspended in H_2O and partitioned successively with EtOAc and *n*-BuOH to yield EtOAc (100 g), *n*-BuOH (83 g), and H_2O (217 g) soluble fractions. The EtOAc-soluble fraction was subjected to chromatography using a Geduran Si-60 (Merck, Darmstadt, Germany) column eluted with EtOAc/*n*-hexane (gradient elution by changing from 5/95 to 100/0) to give fractions 1 (8.7 g), 2 (10.1 g), 3 (11.2 g), 4 (9.3 g), 5 (8.7 g), 6 (9.3 g), 7 (7.5 g), 8 (4.5 g), and 9 (2.2 g). The fractions were further separated by semipreparative HPLC on a model GBC LC-1440 instrument with a 250 × 10.0 mm i.d., 5 μm Luna Si-60 column (Phenomenex, Torrance, CA). Compounds **1** (6.0 mg) and **6** (6.1 mg) were eluted from fraction 1 with 5% EtOAc in *n*-hexane. Compounds **2** (8.1 mg), **3** (4.0 mg), and **7** (6.2 mg) were eluted from fraction 3 with 15% EtOAc in *n*-hexane. Compounds **8** (46.5 mg) and **9** (25.3 mg) were eluted from fraction 4 with 20% EtOAc in *n*-hexane. Compound **4** (7.4 mg) was eluted from fraction 6 with 40% EtOAc in *n*-hexane. Compound **5** (7.0 mg) was eluted from fraction 7 with 60% EtOAc in *n*-hexane.

***O-trans*-Cinnamoylglutinol (1):** white solid; mp 97−98 °C; $[\alpha]^{25}_D$ +59.0 (*c* 0.33, CH_3OH); UV (MeOH) λ_{max} (log ε) 276 (4.59), 221(4.41), 215(4.50) nm; IR (KBr) ν_{max} 2935, 2865, 1709, 1645, 1455, 1385, 1310, 1171 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.61 (1H, d, J = 16.0 Hz, H-3′), 7.48 (2H, m, H-5′, H-9′), 7.36 (3H, m, H-6′, H-7′, H-8′), 6.38 (1H, d, J = 16.0 Hz, H-2′), 5.58 (1H, br d, J = 5.6 Hz, H-6), 4.82 (1H, br t, J = 2.4 Hz, H-3), 1.16 (3H, s, H-28), 1.12 (3H, s, H-26), 1.11 (3H, s, H-23), 1.09 (3H, s, H-24), 1.01 (3H, s, H-27), 0.98 (3H, s, H-30), 0.95 (3H, s, H-29), 0.91 (3H, s, H-25); ^{13}C NMR data, see Table 1; EIMS *m*/*z* 556 [M^+] (8), 408 (100), 393 (31), 341 (11), 283 (23), 274 (86), 259 (70), 218 (24), 205 (22), 187 (15), 173 (19), 131 (33); HREIMS *m*/*z* 556.4271 (calcd for $C_{39}H_{56}O_2$, 556.4266).

22*β*-Hydroxy-12-oleanen-3-one (2): white solid; mp 242−243 °C; $[\alpha]^{25}_D$ +29.1 (*c* 0.50, CH_3OH); IR (KBr) ν_{max} 3476, 2946, 2866, 1699, 1461, 1388, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.26 (1H, t, J = 3.6 Hz, H-12), 3.43 (1H, t, J = 5.2 Hz, H-22), 2.52 (1H, ddd, J = 15.5, 11.0, 7.5 Hz, H_{ax}-2), 2.36 (1H, ddd, J = 15.5, 6.3, 7.5 Hz, H_{eq}-2), 2.09 (1H, br d, J = 14.5 Hz, H-18), 1.11 (3H, s, H-27),1.08 (3H, s, H-23), 1.06 (3H, s, H-25), 1.04 (3H, s, H-24), 1.02 (3H, s, H-30), 0.97 (3H, s, H-26), 0.89 (3H, s, H-29), 0.86 (3H, s, H-28); ^{13}C NMR data, see Table 1; EIMS *m*/*z* 440 [M^+] (8), 234 (100), 219 (44), 216 (21), 176 (24); HREIMS *m*/*z* 440.3650 (calcd for $C_{30}H_{48}O_2$, 440.3642).

15α,16α-Epoxy-12-oleanen-3-ol (3): white solid; mp 251−252 °C; $[\alpha]^{25}_D$ +33.1 (*c* 0.30, CH_3OH); IR (KBr) ν_{max} 3423, 2946, 2926, 2866, 1666, 1461, 1388, 765 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.27 (1H, t, J = 3.6 Hz, H-12), 3.21 (1H, dd, J = 11.6, 4.5 Hz, H-3), 2.89 (1H, d, J = 3.5 Hz, H-15), 2.77 (1H, d, J = 3.5 Hz, H-16), 2.08 (1H, t, J = 12.8 Hz, H_{ax}-19), 1.25 (3H, s, H-27), 0.99 (3H, s, H-23), 0.91 (3H, s, H-26), 0.89 (3H, s, H-28), 0.89 (3H, s, H-25), 0.87 (3H, s, H-29), 0.83 (3H, s, H-30), 0.78 (3H, s, H-24); ^{13}C NMR data, see Table 1; EIMS *m*/*z* 440 [M^+] (29), 425 (35), 410 (29), 392 (24), 379 (12), 232 (86), 217 (24), 207 (58), 190 (35), 189 (31), 175 (31), 121 (24), 108 (100), 95 (27), 81 (26), 69 (33); HREIMS *m*/*z* 440.3649 (calcd for $C_{30}H_{48}O_2$, 440.3642).

29-Hydroxy-12-oleanene-3,22-dione (4): white solid; mp 255−256 °C; $[\alpha]^{25}_D$ +25.4 (*c* 0.55, CH_3OH); IR (KBr) ν_{max} 3436, 2956, 1706, 1699, 1467, 1388, 765 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.33 (1H, t, J = 3.3 Hz, H-12), 3.33, 3.31 (each 1H, d, J = 10.7 Hz, H-29), 2.58 (1H, d, J = 14.1 Hz, H_{ax}-21), 2.53 (1H, ddd, J = 15.4, 11.0, 7.4 Hz, H_{ax}-2), 2.38 (1H, ddd, J = 15.4, 6.5, 3.4 Hz, H_{eq}-2), 2.24 (1H, t, J = 13.8 Hz, H_{ax}-19), 1.21 (3H, s, H-27), 1.08 (3H, s, H-23), 1.06 (3H, s, H-25), 1.04 (3H, s, H-24), 1.01 (3H, s, H-28), 1.00 (3H, s, H-26), 0.86 (3H, s, H-30); ^{13}C NMR data, see Table 1; EIMS *m*/*z* 454 [M^+] (13), 439 (7), 248 (100), 220 (39), 217 (54), 205 (26), 187 (20), 161 (45), 135 (30), 133 (36), 119 (37), 107 (29), 55 (39); HREIMS *m*/*z* 454.3440 (calcd for $C_{30}H_{48}O_3$, 454.3435).

22*β*,29-Dihydroxy-12-oleanen-3-one (5): white solid; mp 258−259 °C; $[\alpha]^{25}_D$ +58.2 (*c* 0.25, CH_3OH); IR (KBr) ν_{max} 3397, 2956, 2933,

2866, 1699, 1476, 1388, 1036, 765 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 5.28 (1H, t, $J = 3.2$ Hz, H-12), 3.48 (1H, dd, $J = 5.2$, 3.3 Hz, H_{eq}-22), 3.25 (2H, s, H-29), 2.52 (1H, ddd, $J = 15.9$, 10.9, 7.4 Hz, H_{ax}-2), 2.36 (1H, ddd, $J = 15.9$, 7.0, 3.7 Hz, H_{eq}-2), 2.15 (1H, br d, $J = 12.3$ Hz, H-18), 1.11 (3H, s, H-27), 1.07 (3H, s, H-23), 1.05 (3H, s, H-25), 1.04 (3H, s, H-30), 1.03 (3H, s, H-24), 1.01 (3H, s, H-26), 0.93 (1H, dd, $J = 13.2$, 3.1 Hz, H_{eq}-19), 0.82 (3H, s, H-28); ^{13}C NMR data, see Table 1; EIMS *m/z* 456 [M^+] (6), 425 (21), 412 (24), 250 (100), 219 (65), 201 (24), 135 (35), 121 (31), 119 (31), 107 (32), 95 (31), 81 (32), 55 (45); HREIMS *m/z* 456.3597 (calcd for $C_{30}H_{48}O_3$, 456.3591).

25-Cycloartene-3,24-dione (6): white solid; mp 128−130 °C; $[\alpha]^{25}_D$ +22.1 (*c* 0.29, CH_3OH); UV (MeOH) λ_{max} (log ε) 261 (3.36), 224 (3.71) nm; IR (KBr) ν_{max} 2944, 2866, 1709, 1678, 1460, 1449, 1382 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 5.94, 5.73 (each 1H, br s, H-26), 1.85 (3H, br s, H-27), 1.08 (3H, s, H-28), 1.02 (3H, s, H-29), 0.97 (3H, s, H-18), 0.88 (3H, s, H-30), 0.87 (3H, d, $J = 5.6$ Hz, H-21), 0.76, 0.55 (each 1H, d, $J = 4.3$ Hz, H-19); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 212.6 (C-3), 202.8 (C-24), 144.6 (C-25), 124.2 (C-26), 52.3 (C-17), 50.2 (C-4), 48.7 (C-14), 48.4 (C-5), 47.9 (C-8), 45.4 (C-13), 37.5 (C-2), 35.8 (C-20), 35.5 (C-15), 34.7 (C-23), 33.4 (C-1), 32.8 (C-12), 31.0 (C-22), 29.5 (C-19), 28.1 (C-7), 26.7 (C-11), 26.0 (C-10), 25.8 (C-16), 22.2 (C-29), 21.5 (C-6), 21.1 (C-9), 20.8 (C-28), 19.3 (C-30), 18.1 (C-18, C-21), 17.7 (C-27); EIMS *m/z* 438 [M^+] (8), 414 (13), 363 (20), 313 (37), 231 (28), 199 (32), 197 (82), 175 (39), 149 (34), 149 (43), 135 (52), 121 (62), 107 (63), 95 (87), 91 (86), 81 (68), 89 (74), 59 (59), 55 (100); HREIMS *m/z* 438.3492 (calcd for $C_{30}H_{46}O_2$, 438.3486).

24ξ-Hydroxy-25-cycloarten-3-one (7): white solid; mp 118−120 °C; $[\alpha]^{25}_D$ +20.8 (*c* 0.43, CH_3OH); IR (KBr) ν_{max} 3423, 2946, 2866, 1706, 1465, 1453, 1368 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 4.90, 4.82 (each 1H, br s, H-26), 4.00 (1H, t, $J = 6.6$ Hz, H-24), 1.70 (3H, br s, H-27), 1.08 (3H, s, H-28), 1.02 (3H, s, H-29), 0.97 (3H, s, H-18), 0.88 (3H, s, H-30), 0.87 (3H, d, $J = 5.6$ Hz, H-21), 0.76, 0.55 (each 1H, d, $J = 4.3$ Hz, H-19); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 216.6 (C-3), 147.5 (C-25), 111.4 (C-26), 76.7 (C-24), 52.2 (C-17), 50.2 (C-4), 48.7 (C-14), 48.4 (C-5), 47.9 (C-8), 45.3 (C-13), 37.5 (C-2), 36.0 (C-15), 35.5 (C-20), 33.4 (C-1), 32.8 (C-12), 31.9 (C-22), 31.5 (C-23), 29.5 (C-19), 28.0 (C-7), 26.7 (C-11), 26.0 (C-10), 25.8 (C-16), 22.2 (C-28), 21.5 (C-6), 21.1 (C-9), 20.8 (C-29), 19.3 (C-30), 18.3 (C-21), 18.1 (C-18), 17.2 (C-27); EIMS *m/z* 440 [M^+] (12), 422 (27), 407 (20), 313 (57), 302 (18), 217 (20), 203 (34), 201 (23), 175 (44), 161 (38), 147 (50), 135 (50), 121 (67), 107 (73), 95 (100), 93 (59), 81 (63), 67 (45), 55 (69); HREIMS *m/z* 440.3649 (calcd for $C_{30}H_{48}O_2$, 440.3642).

2,3-(Methylenedioxy)-4-methoxy-5-methylphenol (8): colorless crystal; mp 132−133 °C; UV (MeOH) λ_{max} (log ε) 281 (3.40) nm; IR (KBr) ν_{max} 3441, 1628, 1510, 1471, 1231, 1060, 1026 cm^{-1}; ^1H and ^{13}C NMR data, see Table 2; EIMS *m/z* 182 [M^+] (100), 167 (90), 137 (33), 69 (29); HREIMS *m/z* 182.0575 (calcd for $C_9H_{10}O_4$, 182.0576).

2,3,6-Trimethoxy-5-methylphenol (9): colorless crystal; mp 128−129 °C; UV (MeOH) λ_{max} (log ε) 276 (3.36) nm; IR (KBr) ν_{max} 3421, 2938, 1605, 1508, 1472, 1233, 1130, 1089; ^1H and ^{13}C NMR data, see Table 2; EIMS *m/z* 198 [M^+] (58), 183 (100), 155 (80), 140 (82), 137 (40); HREIMS *m/z* 198.0885 (calcd for $C_{10}H_{14}O_4$, 198.0888).

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