Pentacyclic Triterpenoids from the Aerial Parts of *Lantana camara*

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Three new pentacyclic triterpenoids, camaryolic acid (1), methylcamaralate (2) and camangeloyl acid (3) and six known compounds β-sitosterol 3-*O*-β-D-glucopyranoside (4), octadecanoic acid (5), docosanoic acid (6), palmitic acid (7), camaric acid (8) and lantanolic acid (9) were isolated from the aerial parts of *Lantana camara*. Structures of the new compounds were elucidated by spectroscopic and chemical methods.

Key words *Lantana camara*; Verbenaceae; pentacyclic triterpenoid; camaryolic acid; methylcamaralate; camangeloyl acid

Lantana camara L. (Verbenaceae) is a hairy shrub, native to tropical America. Different parts of this plant are used for the treatment of various human ailments such as itches, cuts, ulcers, swellings, bilious fever, catarrh, eczema, tetanus, malaria, tumors and rheumatism.[1,2] Phytochemical studies carried out by different groups of workers on different parts of the plant have resulted in the isolation of various terpenoids, steroids and flavonoids.[3—5] In the course of investigations on the constituents of the aerial parts of *L. camara*, three new pentacyclic triterpenoids namely camaryolic acid (**1**), methylcamaralate (**2**) and camangeloyl acid (**3**) were isolated. The structures of these constituents were elucidated as 3,25-epoxy-3α-methoxy-22β-[β,β-dimethylacryloyloxy]-urs-12-en-28-oic acid, methyl 22β-acetoxy-3,25-epoxy-3α-hydroxy-urs-12-en-28-oate and 3,25-epoxy-3α-hydroxy-22β-[(*Z*)-2′-methyl-2′-butenoyloxy]-11-oxoolean-12-en-28-oic acid respectively on the basis of various 2D-NMR techniques including ^{1}H–^{1}H correlation spectroscopy (COSY), nuclear overhauser enhancement spectroscopy (NOESY), heteronuclear multiple quantum coherence (HMQC) and heteronuclear multiple bond connectivity (HMBC). In addition six known compounds β-sitosterol 3-*O*-β-D-glucopyranoside (**4**),[6] octadecanoic acid (**5**),[7] docosanoic acid (**6**),[8] palmitic acid (**7**),[9] camaric acid (**8**)[10] and lantanolic acid (**9**)[11] were isolated from this plant. This is the first report of the isolation of compound **4** from *L. camara.* Herein, we report the structural assignments of the three new triterpenoids.

Results and Discussion

The high resolution electron impact mass spectrum (HR-EI-MS) of **1** showed the M^+ peak at *m/z* 582.3918 corresponding to the molecular formula $C_{36}H_{54}O_6$. Its infrared (IR) spectrum showed absorption bands at 3450—2620 (br, COOH), 1730 (ester carbonyl), 1710 (acid carbonyl) and 1620 cm^{-1} (olefinic double bond). The ^{1}H-NMR spectrum (Table 1) of **1** showed eight methyl signals, four tertiary methyls as singlets (δ_H 0.74, 0.95, 1.00 and 1.05) and two secondary methyls as doublets at δ_H 0.85 (J=6.2 Hz) and δ_H 0.89 (J=6.4 Hz) and two tertiary methyl signals on the double bond. It also exhibited a one-proton doublet at δ_H 2.40 (J=11.2 Hz). These data showed that **1** belongs to the α-amyrin series of pentacyclic triterpenoids, which was confirmed by observing the characteristic[12] signals in the ^{13}C-NMR spectrum (Table 2) at δ_C 125.9 (C-12) and δ_C 138.2 (C-13). Two one-proton double doublets appeared at δ_H 4.26 (J=8.9, 2.7 Hz) and δ_H 3.88 (J=8.9, 1.0 Hz) due to two non-equivalent methylene protons H-25a and H-25b (δ_C 67.7; distortionless enhancement by polarization transfer (DEPT) and HMQC) respectively. Two one-proton triplets at δ_H 5.00 (J=3.0 Hz) (δ_C 75.3; DEPT and HMQC) and δ_H 5.23 (J=3.6 Hz) (δ_C 125.9; DEPT and HMQC) were ascribed to H-22α and H-12 respectively indicating the presence of β-oriented ester side chain at C-22 and a double bond at position 12. It formed methyl ester (**1a**, δ_H 3.50 s) on treatment with diazomethane. Retro–Diels–Alder fragmentation[13] around ring C followed by the loss of the ester side chain in the form of acid, resulted in an ion at *m/z* 246.1599 ($C_{16}H_{22}O_2$) indicating the presence of COOH group at C-14 or C-17. It was placed at C-17 on the basis of ^{13}C-NMR values of ring E which were comparable with those of compounds having similar structures.[14] Further evidence for placing the COOH group at C-17 was provided by the fact that the presence of carboxyl group at C-14[15] has a marked effect on the chemical shifts of C-12, C-13 and C-14 *i.e.* ^{13}C-NMR values of C-12 and C-14 appear downfield and that of C-13 appear upfield as compared to the compounds having COOH group at C-17.[14]

An OMe group which appeared at δ_H 3.23 (δ_C 49.3; DEPT and HMQC) as a three proton singlet in the ^{1}H-NMR spectrum was located at C-3 with α-orientation, since the compound had no further carbinylic proton in the ^{1}H-NMR spectrum and the OMe showed interaction with C-3 (δ_C 100.5) in the HMBC spectrum (Fig. 1). These data showed a close similarity of **1** with camaracinic acid,[14] *i.e.* a β-oriented ketal system at C-3 with C-25, a double bond at C-12, a β-oriented ester side chain at C-22 and a COOH group at C-17 in the α-amyrin skeleton. The mass spectrum of **1** also showed a peak at *m/z* 83.0484, corresponding to C_5H_7O and a peak at *m/z* 482.3372 ($C_{31}H_{46}O_4$), resulting from the loss of 100 mass units from the molecular ion. These observations were indicative of a dimethylacrylic ester-side chain at C-22. Comparison of ^{1}H-NMR spectrum of **1** with that of lantanilic acid[16] indicated that the ester moiety of **1** was similar to that of lantanilic acid as it showed two three-proton singlets at δ_H 1.82 and δ_H 2.10 ascribed to H-4′ and H-5′ respectively and a one-proton singlet at δ_H 5.54 for H-2′ suggesting a β,β-dimethylacrylic acid ester which was also confirmed by ^{13}C-NMR values assigned to this moiety (Table 2) through HMQC and HMBC interactions and DEPT experiment. Interaction of H-22 with C-1′ in the HMBC spectrum confirmed this ester moiety at C-22. The above spectral data characterized **1** as 3,25-epoxy-3α-methoxy-22β-[β,β-dimethylacryloyloxy]-urs-12-en-28-oic acid.

Compound **2** showed the molecular ion peak at *m/z*

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Table 1. ^{1}H-NMR Data (δ/ppm) of **1**—**3**[a]

Proton	**1**[b]	**2**[b]	**3**[b]
1	2.10 (m)	2.00 (m)	2.10 (m)
	1.20 (m)	1.21 (m)	1.20 (m)
2	1.41 (m)	1.40 (m)	1.50 (m)
	1.19 (m)	1.18 (m)	1.32 (m)
5	1.19 (m)	1.19 (m)	1.15 (m)
6	1.51 (m)	1.50 (m)	1.50 (m)
7	1.38 (m)	1.37 (m)	1.37 (m)
9	1.65 (m)	1.68 (m)	2.46 (s)
11	2.12 (m)	2.14 (m)	—
	1.75 (m)	1.70 (m)	—
12	5.23 (t, 3.6)	5.29 (t, 3.6)	5.74 (s)
15	2.14 (m)	2.15 (m)	2.14 (m)
	1.70 (m)	1.72 (m)	1.72 (m)
16	1.85 (m)	1.87 (m)	1.87 (m)
18	2.40 (d, 11.2)	2.41 (d, 10.7)	3.20 (dd, 14.0, 4.2)
19	1.31 (m)	1.30 (m)	1.70 (m)
			1.30 (m)
20	0.96 (m)	0.95 (m)	—
21	1.74 (m)	1.72 (m)	1.80 (m)
			1.50 (m)
22	5.00 (t, 3.0) (α)	5.04 (t, 3.2) (α)	5.12 (t, 3.0) (α)
23	1.00 (s)	1.02 (s)	1.02 (s)
24	0.74 (s)	0.73 (s)	0.71 (s)
25	4.26 (dd, 8.9, 2.7)	4.19 (dd, 8.4, 2.9)	4.50 (dd, 8.3, 2.2)
	3.88 (dd, 8.9, 1.0)	3.85 (dd, 8.4, 1.0)	4.02 (dd, 8.3, 1.1)
26	0.95 (s)	0.93 (s)	0.90 (s)
27	1.05 (s)	1.06 (s)	1.36 (s)
29	0.85 (d, 6.2)	0.86 (d, 6.1)	0.88 (s)
30	0.89 (d, 6.4)	0.88 (d, 6.1)	1.14 (s)
2′	5.54 (s)	1.98 (s)	—
3′	—	—	6.01 (qq, 7.2, 1.5)
4′	1.82 (s)	—	1.94 (dq, 7.2, 1.5)
5′	2.10 (s)	—	1.79 (quintet, 1.5)
3-OCH$_3$	3.23 (s)	—	—
28-OCH$_3$	—	3.46 (s)	—

a) 400 MHz in $CDCl_3$. *b*) Figures in parentheses denote *J* values (Hz). δ in ppm from TMS.

Table 2. ^{13}C-NMR Data (δ/ppm) of **1**—**3**[a]

Carbon	**1**	**2**	**3**
1	35.0	35.1	34.5
2	27.7	28.0	27.9
3	100.5	98.9	99.0
4	38.5	38.5	38.5
5	50.9	50.3	51.1
6	19.7	19.6	19.6
7	31.2	31.2	30.8
8	40.7	40.3	43.7
9	41.9	41.9	55.5
10	34.7	35.0	35.1
11	23.8	23.1	198.4
12	125.9	126.1	127.9
13	138.2	137.3	168.7
14	42.1	42.5	44.0
15	29.7	29.4	29.7
16	24.9	24.9	23.7
17	51.4	51.8	50.4
18	49.3	49.4	39.5
19	39.0	39.3	44.3
20	38.5	38.7	30.1
21	34.6	34.9	37.6
22	75.3	75.7	75.3
23	27.2	27.2	27.4
24	16.9	16.9	17.7
25	67.7	67.9	65.7
26	18.4	18.4	18.9
27	23.4	23.1	23.2
28	178.9	178.0	178.1
29	17.5	17.7	33.6
30	21.0	21.2	25.9
1′	165.3	170.0	166.3
2′	116.0	20.7	127.6
3′	156.8	—	138.8
4′	27.4	—	15.6
5′	20.2	—	20.4
3-OCH$_3$	49.3	—	—
28-OCH$_3$	—	51.2	—

a) 100 MHz in $CDCl_3$. δ in ppm from TMS.

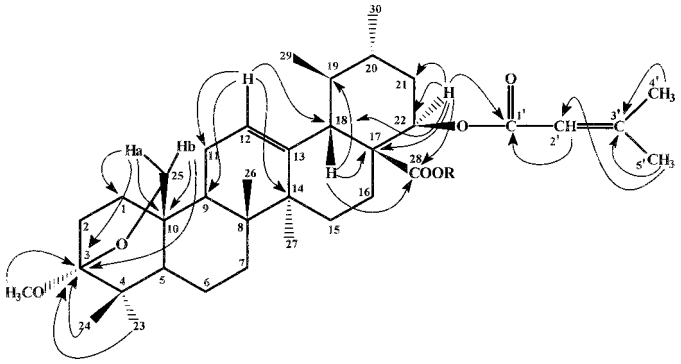

Fig. 1. Significant HMBC Interactions of **1** R=H and **1a** R=CH_3

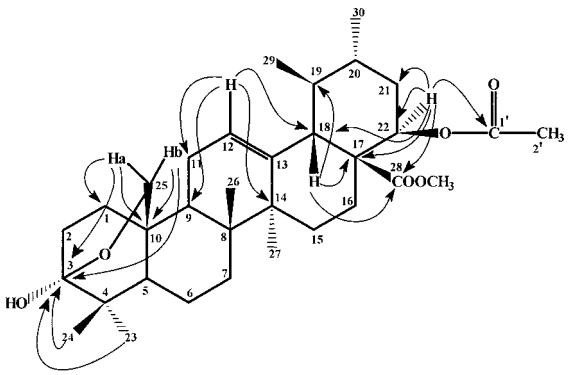

Fig. 2. Significant HMBC Interactions of **2**

542.3900 in the HR-EI-MS corresponding to the molecular formula $C_{33}H_{50}O_6$. Its IR spectrum showed absorption bands at 3450 (OH), 1740 (ester C=O) and 1620 cm^{-1} (C=C). Analysis of the ^{1}H- and ^{13}C-NMR spectra (Table 1, 2) indicated that its structure is similar to that of compound **1** except that it has acetoxy group at C-22 (δ_H 1.98, 3H, s; δ_C 170.0 (C-1′), 20.7 (C-2′)) instead of acryloxy side chain. Further, its ^{1}H-NMR spectrum also showed the presence of OMe group (δ_H 3.46, s; δ_C 51.2; DEPT and HMQC) which was placed at C-28 instead of C-3 due to its interaction observed in the HMBC spectrum (Fig. 2) with C-28 and an α-oriented OH group (3450 cm^{-1}) was located at C-3 instead of OMe. In the light of these observations, the structure of **2** has been elucidated as methyl 22β-acetoxy-3,25-epoxy-3α-hydroxy-urs-12-en-28-oate. Compound **2** is a new natural product, however, its synthesis from camarinic acid has been reported earlier.[10]

Compound **3** showed a molecular ion peak $[M]^+$ at *m*/*z* 582 in its EI-MS, the exact mass measurement (582.3546) of which gave its molecular formula as $C_{35}H_{50}O_7$. Its IR spec-

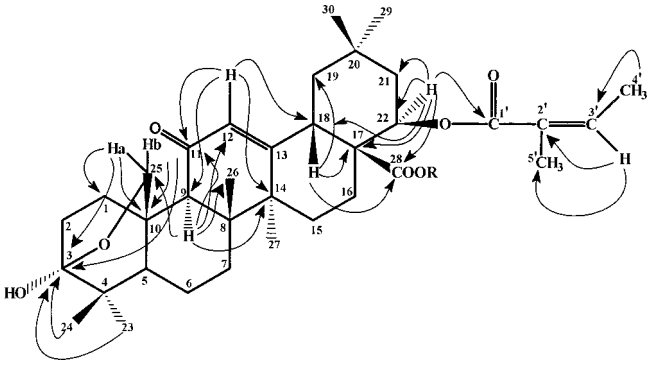

Fig. 3. Significant HMBC Interactions of **3** R=H and **3a** R=CH_3

trum showed absorption bands at 3450—2650 (br, OH, COOH), 2940, 2850 (CH), 1730—1700 (acid and ester C=O), 1690 (α,β unsaturated ketone) and 1620 (C=C). Its ultraviolet (UV) spectrum showed the absorption maximum at 248 nm. The ^{1}H-NMR spectrum (Table 1) showed six three-proton singlets at δ_H 0.71, 0.88, 0.90, 1.02, 1.14 and 1.36, attributable to six tertiary methyls, a one-proton double doublet at δ_H 3.20 (J=14.0, 4.2 Hz) characteristic[14] of H-18 of Δ^{12} oleanene triterpenoids. A β-oriented hemiketal system at C-3 with C-25 was also indicated in compound **3** [δ_H 4.50 (1H, dd, J=8.3, 2.2 Hz, H-25a) and δ_H 4.02 (1H, dd, J=8.3, 1.1 Hz, H-25b)]. It also has a β-oriented ester side chain at C-22 [δ_H 5.12 (1H, t, J=3.0 Hz); δ_C 75.3, HMQC spectrum]. The ^{1}H-NMR [δ_H 6.01 (1H, qq, J=7.2, 1.5 Hz, H-3′); δ_H 1.94 (1H, dq, J=7.2, 1.5 Hz, H-4′); δ_H 1.79 (1H, quintet, J=1.5 Hz, H-5′)] and ^{13}C-NMR spectral data (Table 2) and their correlations in the HMQC spectrum and HMBC connectivities (Fig. 3) indicated the presence of a 2,3-dimethylacrylic acid ester side chain with Z-configuration[17] which was further confirmed by interaction of H-3′ (δ_H 6.01) with 5′-Me (δ_H 1.79) in the NOESY spectrum. The COOH group indicated in the IR spectrum and confirmed by methylation with diazomethane (**3a**, δ_H, 3.51, s) was located at C-17 by comparing the ^{13}C-NMR values of rings C, D and E with those of similar compounds[14] as discussed for compound **1**. These data showed a close similarity of **3** with that of camaric acid.[14] The compound also has an α,β-unsaturated ketonic functionality (1690 cm^{-1}, λ_{max} 248 nm) which was placed at C-11 due to the presence of a one-proton singlet at δ 5.74 (H-12) and ^{13}C-NMR signals[18] at δ_C 198.4 (C-11), 127.9 (C-12) and 168.7 (C-13). Connectivities of H-9 with C-11, C-12, C-14, C-25 and C-26 and of H-12 with C-9, C-11, C-14 and C-18 supported this assignment. The remaining oxygen was placed at C-3 as α-oriented hydroxy group as there is no further carbinylic proton in the NMR spectra. Thus the structure of **3** was established as 3,25-epoxy-3α-hydroxy-22β-[(*Z*)-2′-methyl-2′-butenoyloxy]-11-oxo-olean-12-en-28-oic acid.

Experimental

General The IR spectra were recorded on a JASCO A-302 spectrophotometer. The UV spectra were obtained on a HITACHI-U-3200 spectrophotometer. The EIMS and HREI-MS were recorded on Finnigan MAT-112 and JMS HX-110 spectrometers, respectively. The ^{1}H-NMR spectra were recorded on a Bruker AM-400 FT-NMR spectrometer operating at 400 MHz, while the ^{13}C-NMR spectra were obtained on the same instrument operating at 100 MHz. The chemical shifts are reported in δ (ppm), and the coupling constants are in Hz. HMQC, ^{1}H–^{1}H COSY, NOESY and HMBC were obtained with the usual pulse sequence, and data processing was performed with Xwin-NMR software version 3.0. Silica gel 9385 (Merck) was used for column chromatography (CC) and flash column chromatography (FCC), and Silica gel 60 PF_{254} (Merck) was used for vacuum liquid chromatography (VLC) and thick layer chromatography (TLC).

Plant Material The plant material was collected from the Karachi region in February 1997, and identified as *L. camara* by Mr. Abdul Ghafoor, Department of Botany, University of Karachi. A voucher specimen (No. 63482 KUH) has been deposited in the herbarium of the same university.

Extraction and Isolation Air-dried aerial parts of *L. camara* (10 kg) were repeatedly extracted with MeOH at room temperature. The concentrated extract, obtained on removal of the solvent from the combined extract under reduced pressure was partitioned between EtOAc and H_2O. The EtOAc phase was treated with 4% Na_2CO_3 solution to separate the acidic from the neutral fraction. The EtOAc layer containing the neutral fraction was washed with water, dried (Na_2SO_4), and passed through active charcoal. The charcoal bed was successively washed with EtOAc and MeOH–C_6H_6 (1 : 1), which were combined on the basis of TLC. The residue obtained on removal of the solvent from the charcoal filtrates and washings was divided into hexane-soluble and hexane-insoluble fractions. The hexane-insoluble fraction was again divided into Et_2O-soluble and Et_2O-insoluble portions. The Et_2O-insoluble fraction was again divided into EtOAc-soluble and EtOAc-insoluble portions. The residue (40 g) obtained from the EtOAc-soluble portion was subjected to vacuum liquid chromatography (VLC) ($CHCl_3$; $CHCl_3$–MeOH in order of increasing polarity), which yielded 9 fractions (1—9). Fraction 6 obtained on elution with $CHCl_3$–MeOH (9.5 : 0.5) yielded pure **4** (35.3 mg) as colourless crystallizate. Fraction 1 (26 g) ($CHCl_3$; $CHCl_3$–MeOH, 9.9 : 0.1 eluate) was further subjected to VLC (hexane, hexane–EtOAc, in order of increasing polarity), which ultimately furnished 8 fractions (I to VIII). Fr. II (216 mg) (hexane eluate) was subjected to flash column chromatography (FCC) (hexane, hexane–EtOAc, in order of increasing polarity) which furnished 9 fractions (II-1 to II-9). Fraction II-2 (hexane eluate) on purification through TLC ($CHCl_3$–MeOH, 9.5 : 0.5) gave **5** (5.2 mg). Fraction II-3 (hexane eluate) afforded **6** (16.5 mg). Fraction II-6 obtained on elution with hexane–EtOAc (9 : 1) yielded **7** (3.3 mg).

Fraction III (2.6 g) (hexane–EtOAc, 8 : 2 eluate) was subjected to FCC (hexane, hexane–EtOAc, in order of increasing polarity), which furnished 18 fractions (III-1 to III-18). Fraction III-14 obtained on elution with hexane–EtOAc (9 : 1) gave **1** (9.8 mg). Fraction III-17 (hexane–EtOAc, 9 : 1 eluate) gave two major spots on TLC which on separation through TLC ($CHCl_3$–MeOH, 9.5 : 0.5) afforded **8** (4 mg) and **9** (6 mg). The main fraction 3 (4.7 g) ($CHCl_3$–MeOH, 9.8 : 0.2 eluate) was further subjected to VLC ($CHCl_3$; $CHCl_3$–MeOH in order of increasing polarity), which yielded 9 fractions (3-1 to 3-9). Fraction 3-3 (600 mg) ($CHCl_3$ eluate) was subjected to flash column chromatography (FCC) (hexane, hexane–EtOAc in order of increasing polarity) which furnished 7 fractions (3-3-I to 3-3-VII). Fraction 3-3-VI obtained on elution with hexane–EtOAc (9 : 1) afforded pure **2** (58.1 mg). Fraction 3-3-IV (269.5 mg) was subjected to column chromatography (CC) ($CHCl_3$; $CHCl_3$–MeOH, in order of increasing polarity) which furnished 12 fractions (3-3-IV-1 to 3-3-IV-12). Fraction 3-3-IV-10 obtained on elution with $CHCl_3$–MEOH (9.8 : 0.2) afforded **3** (10.0 mg).

Camaryolic acid (**1**): An amorphous powder; $[\alpha]_D$ +169° (c=0.10, $CHCl_3$); UV λ_{max} (MeOH) nm: 217; IR ($CHCl_3$) cm^{-1}: 3450—2620 (br, COOH), 1730 (ester C=O), 1710 (acid C=O), 1620 (C=C); EI-MS *m/z* (rel. int. %): 582 $[M]^+$ (7), 482 (18), 285 (4), 249 (10), 246 (7), 236 (9), 201 (6), 119 (40), 83 (100), 55 (65); HR-EI-MS *m/z*: 582.3918 (Calcd for $C_{36}H_{54}O_6$, 582.3920), 482.3382 ($C_{31}H_{46}O_4$), 285.1859 ($C_{19}H_{25}O_2$), 249.1850 ($C_{16}H_{25}O_2$), 246.1615 ($C_{16}H_{22}O_2$), 236.1770 ($C_{15}H_{24}O_2$), 201.1650 ($C_{15}H_{21}$), 119.0864 (C_9H_{11}), 83.0484 (C_5H_7O); ^{1}H- and ^{13}C-NMR: see Tables 1 and 2.

Methylation of 1 Compound **1** (5 mg) formed methyl derivative **1a** (4.5 mg) on treatment with an ethereal solution of diazomethane and the usual workup. EI-MS *m/z*: 596 $[M^+]$; ^{1}H-NMR ($CDCl_3$) δ: 0.72 (3H, s, H-24), 0.84 (3H, d, J=6.0 Hz, H-29), 0.88 (3H, d, J=6.2 Hz, H-30), 0.93 (3H, s, H-26), 1.00 (3H, s, H-23), 1.06 (3H, s, H-27), 1.80 (3H, s, H-4′), 2.00 (3H, s, H-5′), 2.41 (1H, d, J=11.0 Hz, H-18), 3.24 (3H, s, 3-OMe) 3.50 (3H, s, COOMe), 3.85 (1H, dd, J=8.8, 1.0 Hz, H-25b), 4.25 (1H, dd, J=8.8, 2.6 Hz, H-25a), 5.01 (1H, t, J=3.2 Hz, H-22α), 5.20 (1H, t, J=3.5 Hz, H-12), 5.53 (1H, s, H-2′).

Methylcamaralate (**2**): An amorphous powder; $[\alpha]_D$ +171° (c=0.12, $CHCl_3$); UV λ_{max} (MeOH) nm; 210; IR ($CHCl_3$) cm^{-1}: 3450 (OH), 1740 (ester C=O), 1620 (C=C); EI-MS *m/z* (rel. int. %): 542 $[M]^+$ (2), 482 (17), 299 (5), 260 (8), 201 (38), 185 (16), 133 (17), 119 (53), 105 (19), 69 (100); HR-EI-MS *m/z*: 542.3900 (Calcd for $C_{33}H_{50}O_6$, 542.3912), 482.3389

($C_{31}H_{46}O_4$), 299.2014 ($C_{20}H_{27}O_2$), 260.1774 ($C_{17}H_{24}O_2$), 201.1638 ($C_{15}H_{21}$), 185.1328 ($C_{14}H_{17}$), 133.1015 ($C_{10}H_{13}$), 119.0858 (C_9H_{11}), 105.0702 (C_8H_9), 69.0701 (C_5H_9); ^{1}H- and ^{13}C-NMR: see Tables 1 and 2.

Camangeloyl acid (**3**): An amorphous powder; $[\alpha]_D$ +165° (c=0.15, $CHCl_3$); UV λ_{max} (MeOH) nm: 248; IR ($CHCl_3$) cm^{-1}: 3450—2650 (br, OH, COOH), 2940, 2850 (CH), 1730—1700 (acid and ester C=O), 1690 (α,β unsaturated ketone), 1620 (C=C); EI-MS *m/z* (rel. int. %): 582 $[M]^+$ (2), 564 (17), 519 (96), 482 (4), 466 (15), 419 (98), 260 (4), 242 (3), 185 (16), 133 (30), 119 (53), 105 (40), 55 (100); HR-EI-MS *m/z*: 582.3546 (Calcd for $C_{35}H_{50}O_7$, 582.3556), 564.3448 ($C_{35}H_{48}O_6$), 519.3470 ($C_{34}H_{47}O_4$), 482.3028 ($C_{30}H_{42}O_5$), 466.3078 ($C_{30}H_{42}O_4$), 419.2945 ($C_{29}H_{39}O_2$), 260.1410 ($C_{16}H_{20}O_3$), 242.1301 ($C_{16}H_{18}O_2$), 185.1329 ($C_{14}H_{17}$), 133.1018 ($C_{10}H_{13}$), 119.0859 (C_9H_{11}), 105.0706 (C_8H_9); ^{1}H- and ^{13}C-NMR: see Tables 1 and 2.

Methylation of 3 Compound **3** (8 mg) afforded methyl derivative **3a** (7.0 mg) on treatment with an ethereal solution of diazomethane and the usual workup. EI-MS *m/z*: 596 $[M^+]$; ^{1}H-NMR ($CDCl_3$) δ: 0.72 (3H, s, H-24), 0.87 (3H, s, H-29), 0.92 (3H, s, H-26), 1.02 (3H, s, H-23), 1.12 (3H, s, H-30), 1.34 (3H, s, H-27), 1.78 (3H, quintet, J=1.4 Hz, H-5′), 1.94 (3H, dq, J=7.0, 1.4 Hz, H-4′), 3.22 (1H, dd, J=14.2, 4.1 Hz, H-18), 3.51 (3H, s, COOMe), 4.01 (1H, dd, J=8.2, 1.0 Hz, H-25b), 4.51 (1H, dd, J=8.2, 2.0 Hz, H-25a), 5.13 (1H, t, J=3.2 Hz, H-22α), 5.73 (1H, s, H-12), 6.00 (1H, qq, J=7.0, 1.4 Hz, H-3′).

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