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TWO NEW PENTACYCLIC TRITERPENOIDS FROM THE AERIAL PARTS OF *LANTANA CAMARA* LINN

Bina S. Siddiqui, Aneela Wahab, and Sabira Begum*

H. E. J. Research Institute of Chemistry, University of Karachi, Karachi-75270, Pakistan

Abstract– Two new constituents camarolide (**1**) and lancamaric acid (**4**) along with two known compounds oleanonic acid (**2**) and ursonic acid (**3**) have been isolated from the aerial parts of *Lantana camara* Linn. Structures of the new compounds have been established as 3-keto-urs-11-en-13β(28)-olide (**1**) and 3,25-epoxy-3α-ethoxy-olean-12-en-28-oic acid (**4**) through spectral studies including 1D (^{1}H-, ^{13}C-NMR) and 2D (COSY-45, NOESY, *J*-resolved, HMQC and HMBC) NMR.

Lantana camara L. (Verbenaceae) commonly known as lantana is a hairy shrub, native of tropical America and cultivated as an ornamental or hedge plant. Its different parts are reputed to be of use in traditional medicine for the treatment of various human ailments such as ulcers, eczema eruptions, malaria and rheumatism.[1] Pharmacological investigations have indicated that extracts of the shoots of *L. camara* exhibit antibacterial properties.[1] Lancamarone, a steroid from the leaves, possesses cardiotonic properties, while lantamine, an alkaloid from the stem and root bark, shows strong antipyretic and antispasmodic properties comparable with those of quinine.[1,2] Phytochemical studies undertaken by different groups of workers on different parts of the plant have resulted in the isolation of various steroids, terpenoids, and flavonoids.[3-5] In view of the pharmacological properties of *L. camara*, the present studies were undertaken on the chemical constituents of the aerial parts of this plant, which resulted in the isolation and structure elucidation of two new pentacyclic triterpenoids, camarolide (**1**) and lancamaric acid (**4**), and two known compounds, oleanonic acid (**2**) and ursonic acid (**3**)

RESULTS AND DISCUSSION

The molecular formula of compound (**1**), $C_{30}H_{44}O_3$ (M^+ 452.3268), was obtained through HREIMS. Its IR spectrum showed bands at 2920, 2850 (CH), 1755 (lactone C=O), 1700 (ketone C=O), 1620 (C=C) and 1130 cm^{-1} (C-O). The UV spectrum showed absorption band at 210 nm indicating the lack of conjugation in the molecule. The ^{1}H- and ^{13}C-NMR data of **1** indicated that it belongs to α-amyrin type of triterpenoids. Thus its ^{1}H-NMR spectrum showed five tertiary methyl signals at δ 0.93, 1.02, 1.04, 1.08 and 1.16 and two secondary methyls at δ 0.92 (d, *J*=6.3 Hz) and 0.99 (d, *J*=6.2 Hz). It further showed two olefinic (1620 cm^{-1}) one-proton double doublets at δ 5.95 (*J*=10.5, 1.3 Hz) and 5.57 (*J*=10.5, 3.0 Hz) correlated with δ_C 132.7 (C-11) and δ_C 129.4 (C-12) respectively[6] in the HMQC spectrum and assigned to H-11 and H-12 respectively (Table 1). These protons showed connectivities with H-9 in the COSY-45 spectrum (Figure 1). These assignments were confirmed through HMBC interactions (Figure 2). It may be noted that H-12 showed larger coupling (*J*=3.0 Hz) with H-9 as the allylic CH (at C-9) bond is perpendicular to the C=C plane, whereas coupling between H-9 and H-11 is smaller (*J*=1.3 Hz) as the dihedral angle between these CH bonds is about 90^o as observed in the Dreiding model of the molecule.[7] The presence of quaternary carbon signals in the ^{13}C-NMR spectrum (br band) at δ 89.2 (C-13) and δ 179

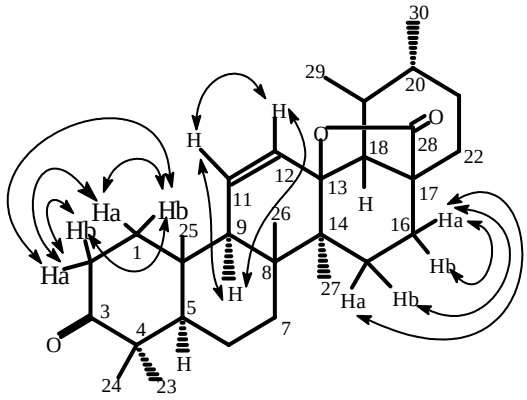

Figure 1. Significant ^{1}H, ^{1}H COSY Interactions of Camarolide (**1**)

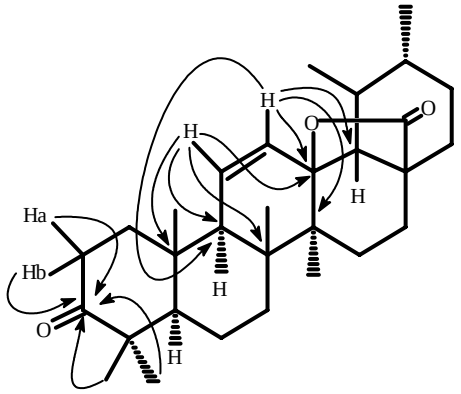

Figure 2. Significant HMBC Interactions of Camarolide (**1**)

(C-28) along with a prominent M^{+}-CO_2 peak at *m/z* 408.3268 in the HREIMS indicated a lactone moiety (1755 cm^{-1}) between C-13 and C-28.[8] The peaks at *m/z* 202.1658 and 69.0687 in the HREIMS confirmed this moiety[9] (Figure 3). The IR spectrum (1700 cm^{-1}) and ^{13}C NMR signal (δ_C 217.5, br band) also indicated[10] the presence of a carbonyl group in the molecule which was placed at C-3 on biogenetic grounds, and verified by the presence of down field signals[10] at δ 2.61 (1H, m, H-2a) and δ 2.43 (1H, m, H-2b) and connectivities of the carbonyl carbon (δ_C 217.5) with H-2a, H-2b, as well as with H-23 and H-24 (Figure 2). From the data recorded above the structure of **1** was elucidated as 3-keto-urs-11-en-13β(28)-olide. It may be noted that δ_C values assigned to C-11 and C-12 of **1** were comparable with those of reported values[6] for ursolic acid lactone acetate whereas δ_H values, unambiguously assigned to these protons in the present studies on the basis of HMQC and HMBC experiments are reverse from the reported values.[6] Compound (**1**) has been synthesized earlier from ursolic acid.[11,12]

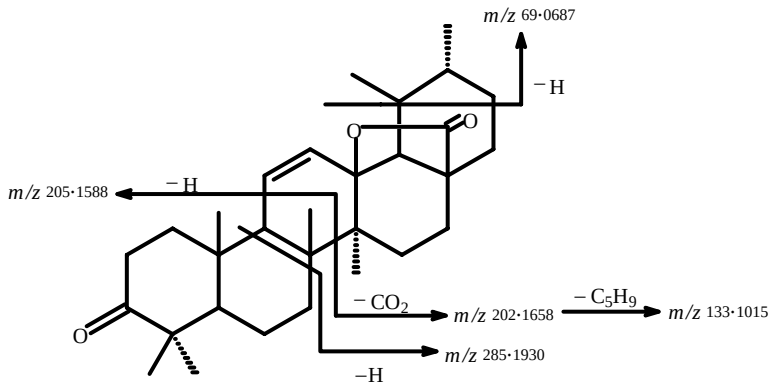

Figure 3. Significant Mass Fragmentation of Camarolide (**1**)

Table 1. ^{1}H- and ^{13}C- NMR Spectral Data of Compound (**1**) ($CDCl_3$).

	δ_C	DEPT	δ_H	m	*J* (Hz)		δ_C	DEPT	δ_H	m	*J* (Hz)
1	39.7	CH_2	2.06 (1a) 1.45 (1b)	m m	-	16	22.8	CH_2	2.10 (16a) 1.40 (16b)	m m	-
2	34.1	CH_2	2.61 (2a) 2.43 (2b)	m m	-	17	45.0	C	-	-	-
3	217.5	C	-	-	-	18	60.7	CH	1.64	d	12.0
4	47.3	C	-	-	-	19	38.2	CH	1.78	m	-
5	54.8	CH	0.83	m	-	20	40.3	CH	0.87	m	-
6	17.2	CH_2	1.58	m	-	21	30.9	CH_2	1.57	m	-
7	31.2	CH_2	1.56	m	-	22	31.4	CH_2	1.84	m	-
8	41.6	C	-	-	-	23	26.1	CH_3	1.08	s	-
9	51.9	CH	2.04	dd	3.0, 1.3	24	20.8	CH_3	1.02	s	-
10	36.4	C	-	-	-	25	19.6	CH_3	0.93	s	-
11	132.7	CH	5.95	dd	10.5, 1.3	26	19.1	CH_3	1.04	s	-
12	129.4	CH	5.57	dd	10.5, 3.0	27	16.1	CH_3	1.16	s	-
13	89.2	C	-	-	-	28	179.0	C	-	-	-
14	42.5	C	-	-	-	29	17.8	CH_3	0.99	d	6.2
15	25.6	CH_2	1.72 (15a) 1.20 (15b)	m m	-	30	18.1	CH_3	0.92	d	6.3

Assignments are based on ^{1}H, ^{1}H COSY, NOESY, *J*-resolved, HMQC and HMBC experiments.

The molecular formula, $C_{32}H_{50}O_4$, of compound (**4**) was obtained through HREIMS (M^+, 498.3677). It showed IR absorption bands at 3450-2650 (br, COOH), 1700 (acid C=O) and 1620 (C=C) cm^{-1} while its UV spectrum showed an absorption maximum at 205 nm. The ^{1}H-NMR spectrum showed six three-proton singlets at δ 0.74, 0.88, 0.97, 1.01, 1.05 and 1.10 attributable to six methyls located on quaternary carbons. It also displayed resonances for an olefinic proton (δ 5.27, t, *J*=3.5 Hz, H-12) and a characteristic[13] methine proton at δ 2.81 (dd, *J*=13.8, 4.4 Hz, H-18) (Table 2). These data along with the characteristic ^{13}C-NMR chemical shifts of C-12 and C-13 at δ 122.6 and 143.6, respectively[14] suggested that **4** belongs to the Δ^{12} β–amyrin series of pentacyclic triterpenoids. Compound (**4**) formed the methyl derivative (**4a**) (δ OMe 3.57) on reaction with diazomethane confirming the carboxyl function indicated by the IR spectrum. The comparable ^{13}C-NMR data[15,16] of ring D and E with similar skeletons having COOH group at C-17 as well as characteristic retro-Diels-Alder fragments[9] of **4** at *m/z* 248.1794, 203.1786 and 133.1011 (Figure 4) indicated the location of the carboxylic group at C-17 and the remaining oxygen function in ring A/B. Furthermore, the ^{1}H-NMR spectrum exhibited a pair of double doublets centred at δ 4.26 (*J*=8.4, 2.3 Hz) and 3.86 (*J*=8.4, 1.1 Hz) for the two non-equivalent methylene protons of the 3,25 epoxy function. This region of the ^{1}H-NMR spectrum showed a close similarity with that of lantanilic acid,[17] thus ascribing these signals to H-25a and H-25b. These assignments were confirmed from cross peaks in the ^{1}H-^{1}H-COSY spectrum (Figure 5), which showed interactions between H-25a and H-25b and the interactions of both these protons with H-1b showing a long range coupling of these protons with H-1 as suggested[17] earlier by various authors for this system.

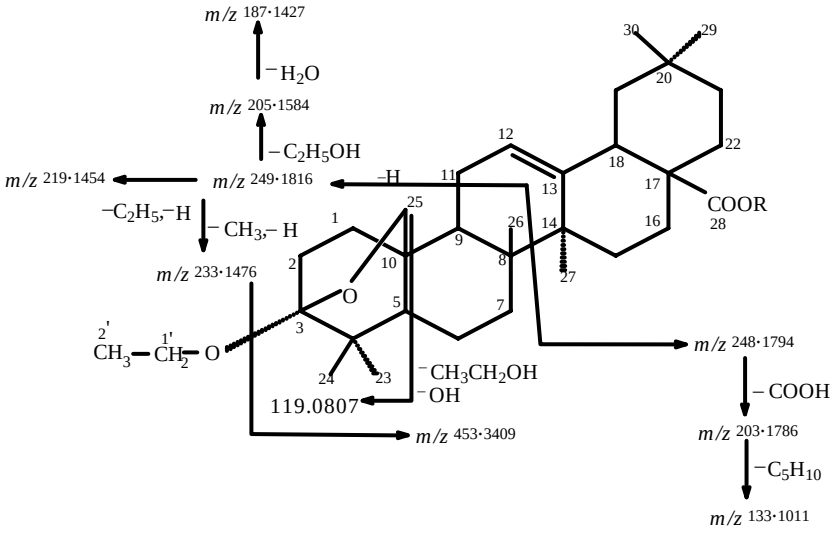

Figure 4. Significant Mass Fragmentation of Lancamaric Acid (**4**), R=H
4a, R= CH_3

The ^{1}H- NMR spectrum showed the presence of an ethoxy group (δ 3.71, 2H, q, *J*=7.0 Hz, H-1′; δ 1.00, 3H, t, *J*=7.0 Hz, H-2′) which was confirmed by the ^{13}C-NMR (DEPT) and HMQC interactions (Table 2). It was located at C-3 since the compound had no further carbinylic proton in the ^{1}H-NMR spectrum and was supported by fragments at *m/z* 249.1816, 205.1584 and 187.1427 (Figure 4) in the mass spectrum and by interactions of H-1′ with C-3 (δ 100.4) in the HMBC spectrum. The HMBC spectrum also showed interactions of H-25b, H-23 and H-24 with C-3 (Figure 6). Therefore, the remaining oxygen function was placed in ring A as a part of ketal structure. Since the carbon (C-25) forming the epoxide linkage with C-3 is β oriented, the ethoxy group was given an α–disposition. In the light of these observations, the structure of **4** has been established as 3,25-epoxy-3α-ethoxy-olean-12-en-28-oic acid.

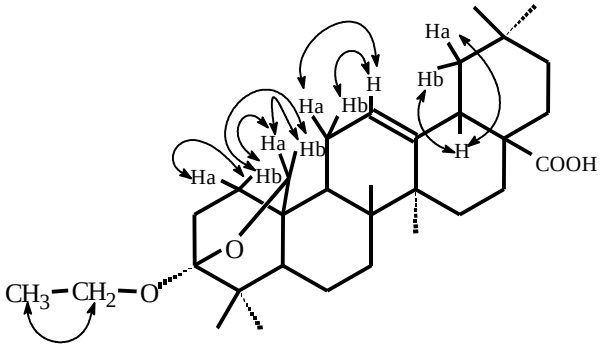

Figure 5. Significant ^{1}H,^{1}H COSY Interactions of Lancamaric Acid (**4**)

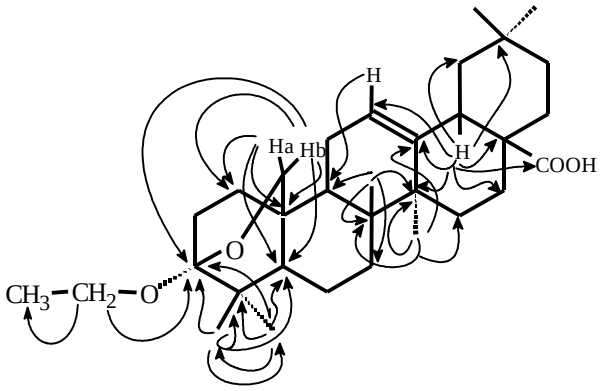

Figure 6. Significant HMBC Interactions of Lancamaric Acid (**4**)

The known compounds (**2**) and (**3**) have been identified through comparison of their spectral data with those of the corresponding constituents reported in literature.[11,18] However, the ^{1}H-NMR (at 500 MHz) and ^{13}C-NMR (at 125 MHz) assignments of **2** are reported for the first time. The ^{13}C-NMR assignments are based on comparison with published values of its methyl ester.[19] Moreover, it is important to note in this context that in the reported[20] ^{1}H-NMR data of **3** assignment of seven three-proton methyl singlets have been made instead of five singlets and two doublets of secondary methyls. In the same reference,

^{13}C-NMR data shows twenty eight carbons instead of thirty carbons without exact assignments. It has been reported that **2** and **3** inhibit the growth of mouse melanoma cells in cultures[21] and *Herpes simplex* virus type I and II *in vitro*.[20,22]

Table 2. ^{1}H- and ^{13}C- NMR Spectral Data of Compound (**4**) ($CDCl_3$).

	δ_C	DEPT	δ_H	m	*J* (Hz)		δ_C	DEPT	δ_H	m	*J* (Hz)
1	34.6	CH_2	2.10 (1a)	m	-	17	46.5	C	-	-	-
			1.20 (1b)								
2	27.7	CH_2	1.40 (2a)	m	-	18	41.1	CH	2.81	dd	13.8,
			1.20 (2b)								4.4
3	100.4	C	-	-	-	19	45.9	CH_2	1.60 (19a)	m	-
									1.15 (19b)	m	-
4	38.5	C	-	-	-	20	30.6	C	-	-	-
5	50.9	CH	1.15	m	-	21	33.8	CH_2	1.24	m	-
6	19.6	CH_2	1.48	m	-	22	32.5	CH_2	1.23	m	-
7	30.7	CH_2	1.37	m	-	23	27.3	CH_3	1.01	s	-
8	40.2	C	-	-	-	24	17.7	CH_3	0.94	s	-
9	41.8	CH	1.72	m	-	25	67.8	CH_2	4.26 (25a)	dd	8.4, 2.3
									3.86 (25b)	dd	8.4, 1.1
10	35.1	C	-	-	-	26	18.4	CH_3	0.74	s	-
11	23.4	CH_2	2.00	-	-	27	25.9	CH_3	1.06	s	-
			1.76	-	-						
12	122.6	CH	5.27	t	3.5	28	181.0	C	-	-	-
13	143.6	C	-	-	-	29	33.0	CH_3	0.88	s	-
14	42.0	C	-	-	-	30	23.6	CH_3	1.09	s	-
15	27.7	CH_2	1.05 (15a)	m	-	1’	65.0	CH_2	3.71	q	7.0
			0.90 (15b)	m	-						
16	23.8	CH_2	1.86	m	-	2’	15.0	CH_3	1.00	t	7.0

Assignments are based on ^{1}H, ^{1}H COSY, NOESY, *J*-resolved, HMQC and HMBC experiments.

EXPERIMENTAL

Melting points were measured with a Gallenkamp melting point apparatus and are uncorrected. UV and IR spectra were recorded on Hitachi-U-3200 and JASCO A-302 spectrometers, respectively. MS spectra were recorded with Finnigan MAT 112 and 312 double focusing mass spectrometers connected to a PDP 11/34 computer system. ^{1}H- and ^{13}C-NMR were measured with a Bruker AM-500 FT-NMR spectrometer operating at 500 MHz for ^{1}H-NMR and 125 MHz for ^{13}C-NMR.The spectra were referenced to the residual solvent signals. The chemical shifts are reported in δ (ppm) and the coupling constants (*J*) are in Hz. For vacuum liquid chromatography (VLC) and flash column chromatography (FCC) silica gel PF_{254} (E. Merck) and silica gel 9385 (E. Merck) respectively were used, while for TLC and preparative TLC silica gel PF_{245} (E. Merck) was used. Hexane used was of the boiling range 60-80^{o}C.

Plant material: Aerial parts of *Lantana camara* were collected from the Karachi region. The plant was identified by Mr. Abdul Ghafoor, Senior Taxonomist, Department of Botany, University of Karachi and a voucher specimen (No. 63482 KUH) is deposited in the Herbarium.

Extraction and Isolation: Air dried aerial parts of *Lantana camara* (10 kg) were extracted with MeOH (20 L) thrice at rt for 48 h. The concentrated extract (1.35 kg), obtained on removal of the solvent from the combined extracts under reduced pressure, was taken in H_2O (5 L) and extracted with EtOAc (15 L) successively. The EtOAc phase gave acidic and neutral fractions on treatment with 4% aqueous Na_2CO_3 and usual work-up. The neutral fraction (129 g) was divided into hexane-soluble and hexane-insoluble

fractions. The hexane-insoluble fraction (66 g) was again divided into Et_2O-soluble and Et_2O-insoluble portions. The Et_2O-soluble fraction (17.5 g) was again divided into hexane soluble and hexane insoluble portions. The residue (3.4 g) obtained from this hexane soluble portion on removal of the solvent, was subjected to VLC (hexane and hexane-EtOAc, in order of increasing polarity) which furnished 7 fractions (Fr-1 to Fr-7). The residue (1.2 g) obtained from the main fraction Fr-2 (hexane-EtOAc 9.5:0.5 eluate) was subjected to FCC (hexane and hexane-EtOAc, in order of increasing polarity) which furnished 12 fractions (Fr-2-1 to Fr-2-12). Fr-2-2 obtained on elution with hexane-EtOAc (9.5:0.5) afforded pure camarolide (**1**) (16 mg) as colorless crystals. Fr-2-5 also obtained on elution with hexane-EtOAc (9.5:0.5) yielded oleanonic acid (**2**) (11.5 mg) as colorless crystals. Fr-2-7 (hexane-EtOAc 9:1 eluate) afforded ursonic acid (**3**) (9.6 mg) as colorless crystals.

The residue (40 g) obtained from the ether insoluble fraction, was subjected to VLC ($CHCl_3$ and $CHCl_3$-MeOH in order of increasing polarity) which furnished 9 fractions (Fr-1 to Fr-9). The residue (26 g) obtained from Fr-1 ($CHCl_3$ and $CHCl_3$-MeOH 9.9:0.1 eluate) was further subjected to VLC (hexane and hexane-EtOAc, in order of increasing polarity) which furnished 8 fractions (Fr-I to Fr-VIII). The residue (2.6 g) obtained from Fr-II (hexane-EtOAc 8:2 eluate) was subjected to FCC (hexane and hexane-EtOAc, in order of increasing polarity) which furnished 18 fractions (Fr-II-1 to F-II-18). Fr-II-10 obtained on elution with hexane-EtOAc (9:1) afforded pure lancamaric acid (**4**) (12.1 mg) as colorless crystals.

Camarolide (**1**): Colorless needles, mp 204-205 ^oC (MeOH). UV λ_{max} (MeOH) nm: 210; IR ν_{max} (KBr) cm^{-1}: 2920, 2850 (CH), 1755 (lactone C=O), 1700 (ketone C=O), 1620 (C=C) and 1130 (C-O). EI-MS *m/z* (rel. int., %) 452 (M^+,78), 408 (100), 391 (17), 285 (20), 246 (10), 205 (32), 202 (27), 133 (37), 69 (55); HREIMS *m/z*: 452.3298, (calcd for $C_{30}H_{44}O_3$, 452.3290), 408.3367 ($C_{29}H_{44}O$), 285.1930 ($C_{19}H_{25}O_2$), 205.1588 ($C_{14}H_{21}O$), 202.1658 ($C_{15}H_{22}$), 133.1015 ($C_{10}H_{13}$), 69.0687 (C_5H_9); ^1H- and ^{13}C-NMR data: see Table 1.

Oleanonic acid (**2**): ^1H-NMR ($CDCl_3$, δ): 5.27 (1H, t, *J*=3.5 Hz, H-12), 2.80 (1H, dd, *J*=14.0, 4.5 Hz, H-18), 2.52 (1H, m, H-2a), 2.35 (1H, m, H-2b), 1.11 (3H, s, CH_3), 1.06 (3H, s, CH_3), 1.02 (3H,s, CH_3), 0.99 (3H, s, CH_3), 0.90 (3H, s, CH_3), 0.87 (3H, s, CH_3), 0.79 (3H, s, CH_3); ^{13}C-NMR ($CDCl_3$, δ): 39.1 (C-1), 34.1 (C-2), 217.7 (C-3), 47.4 (C-4), 55.3 (C-5), 19.6 (C-6), 32.2 (C-7), 39.5 (C-8), 46.9 (C-9), 36.8 (C-10), 22.9 (C-11), 122.3 (C-12), 143.6 (C-13), 41.7 (C-14), 27.7 (C-15), 23.5 (C-16), 46.6 (C-17), 41.0 (C-18), 45.8 (C-19), 30.5 (C-20), 33.8 (C-21), 32.2 (C-22), 26.5 (C-23), 21.4 (C-24), 15.0 (C-25), 16.9 (C-26), 25.8 (C-27), 184.1 (C-28), 33.0 (C-29), 23.6 (C-30).

Lancamaric acid (**4**): Colorless needles, mp 189-190 ^oC (MeOH). UV λ_{max} (MeOH) nm: 205; IR ν_{max} (KBr) cm^{-1}: 3450-2650 (br, COOH), 2920, 2810 (CH), 1700 (acid C=O)and 1620 (C=C). EI-MS *m/z* (rel. int., %) 498 (M^+, 12), 453 (6), 452 (10), 248 (100), 205 (8), 203 (45), 133 (22), 119 (16); HREIMS *m/z*: 498.3701, (calcd for $C_{32}H_{50}O_4$, 498.3708), 453.3409 ($C_{30}H_{45}O_3$), 249.1816 ($C_{16}H_{25}O_2$), 248.1794 ($C_{16}H_{24}O_2$), 233.1476 ($C_{15}H_{21}O_2$), 205.1584 ($C_{14}H_{21}O$), 203.1786 ($C_{15}H_{23}$), 219.1454 ($C_{14}H_{19}O_2$), 187.1427 ($C_{14}H_{19}$), 133.1011 ($C_{10}H_{13}$), 119.0807 (C_9H_{11}); ^1H- and ^{13}C- NMR data: see Table 2.

Methylation of **4**: Compound (**4**) formed **4a** as a colorless crystalline substance on treatment with an ethereal solution of diazomethane in cold and keeping the reaction mixture at rt overnight followed by the usual work up: colorless needles, mp 124-125 ^oC (MeOH). UV λ_{max} (MeOH) nm: 205; IR ν_{max} (KBr) cm^{-1}: 2940, 2840 (CH), 1730 (ester C=O) and 1620 (C=C). EI-MS *m/z* (rel. int., %) 512 (M^+, 13), 453 (8), 452 (9), 262 (100), 205 (6), 203 (43), 133 (20), 119 (18); HREIMS *m/z*: 512.3861 (calcd for $C_{33}H_{52}O_4$, 512.3865), 453.3410 ($C_{30}H_{45}O_3$), 249.1815 ($C_{16}H_{25}O_2$), 262.1932 ($C_{17}H_{26}O_2$), 233.1478 ($C_{15}H_{21}O_2$), 205.1585 ($C_{14}H_{21}O$), 203.1788 ($C_{15}H_{23}$), 219.1456 ($C_{14}H_{19}O_2$), 187.1429 ($C_{14}H_{19}$), 133.0998 ($C_{10}H_{13}$), 119.0807 (C_9H_{11}); ^1H-NMR ($CDCl_3$, δ): 5.26 (1H, t, *J*= 3.4 Hz, H-12), 4.25 (1H, dd, *J*= 8.3, 2.4 Hz, H-25a), 3.87 (1H, dd, *J*=8.3, 1.0 Hz, H-25b), 3.70 (2H, q, *J*= 7.0 Hz, H-1′), 2.80 (1H, dd, *J*= 14.0, 4.4 Hz, H-18), 1.08 (3H, s, CH_3), 1.05 (3H, s, CH_3), 1.02 (3H, s, CH_3), 1.10 (3H, t, *J*= 7.0 Hz, H-2′), 0.93 (3H, s, CH_3), 0.87 (3H, s, CH_3), 0.75 (3H, s, CH_3).

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