



PENTACYCLIC TRITERPENOIDS FROM *LANTANA CAMARA*

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(Received in revised form 18 July 1994)

Key Word Index—*Lantana camara*; Verbenaceae; pentacyclic triterpenoids; 22 β -acetoxy-3,25-epoxy-3 α -hydroxy-12-ursen-28-oic acid; 3,25-epoxy-3 α -hydroxy-22 β (2-methyl-2Z-butenoyloxy)-12-oleanen-28-oic acid.

Abstract—Seven pentacyclic triterpenoids, camarinic acid, camaric acid, oleanolic acid, pomolic acid, lantanolic acid, lantanilic acid and lantic acid, have been isolated from the aerial parts of *Lantana camara*. The two new constituents, camarinic acid and camaric acid, have been characterized as 22 β -acetoxy-3,25-epoxy-3 α -hydroxy-12-ursen-28-oic acid and 3,25-epoxy-3 α -hydroxy-22 β (2-methyl-2Z-butenoyloxy)-12-oleanen-28-oic acid, respectively. The structures of the new acids and lantanilic acid have been elucidated through extensive 1D and 2D NMR studies (COSY-45, NOESY, *J*-resolved, hetero-COSY), while those of the remainder rest on comparisons of their spectral data with the values reported in the literature.

INTRODUCTION

Lantana camara Linn is a hairy shrub, native of tropical America. It is cultivated as an ornamental or hedge plant. Different parts of the plant are used in folklore remedies and traditional systems of medicine for the treatment of various human ailments. The leaves are used in the treatment of itches, cuts, ulcers, swellings, bilious fever, catarrh, eczema and rheumatism. The leaf oil is useful as an antiseptic for wounds. The roots are used for the treatment of toothache and the flowers for chest complaints of children [1]. The plant is considered vulnerary, diaphoretic and carminative. It is also useful for the treatment of fistulae, pustules and tumours as well as tetanus, malaria and atoxy of the abdominal viscera. Pharmacological investigations indicated that extracts of the shoot of *L. camara* exhibit antibacterial properties. Lancamarone, a steroid from the leaves, possesses cardiotonic properties, while lantamine an alkaloid from the bark of stems and roots shows strong antipyretic and antispasmodic properties comparable with those of quinine [2]. Phytochemical studies undertaken by different groups of workers, on different parts of the plant, have resulted in the isolation of various terpenoids [3], steroids [4] and alkaloids [5]. In the light of the medicinal properties attributed to *L. camara*, the present studies were undertaken on the chemical constituents of the aerial parts of this plant, resulting in the isolation and

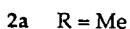
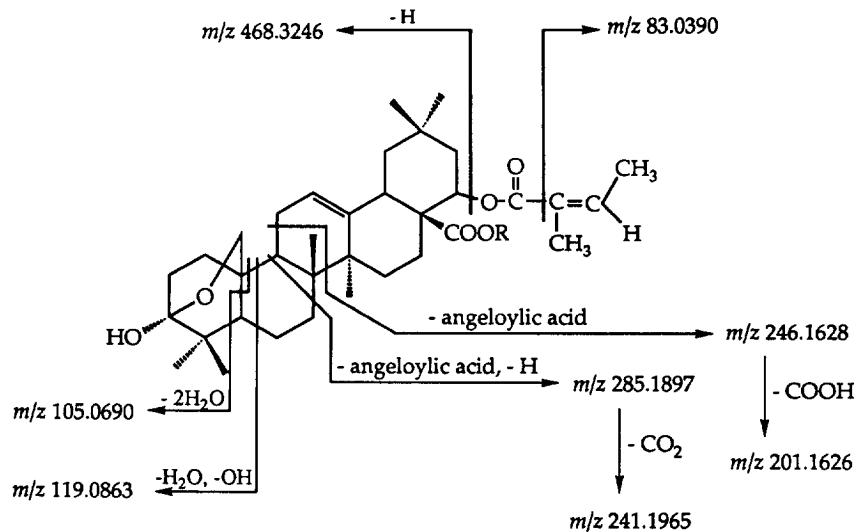
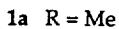
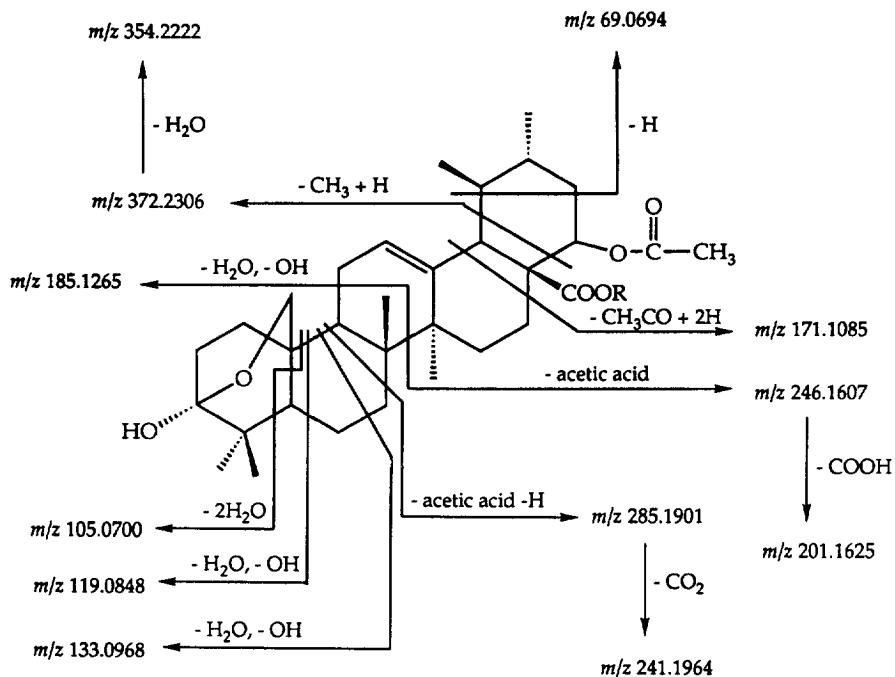
structure elucidation of two new (**1** and **2**) and five known (**3**–**7**) terpenoids. Compounds **3** and **4** are hitherto unreported from this source.

RESULTS AND DISCUSSION

Camarinic acid (**1**) was assigned the molecular formula C₃₂H₄₈O₆ (EI-, FD- and HR-mass spectra). It showed IR absorption bonds at 3500–2600 (br, OH and CO₂H), 1738–1680 (acid and ester carbonyls) and 1620 cm⁻¹ (C=C) while its UV spectrum showed an absorption maximum at 210 nm. The ¹H NMR spectrum displayed resonances for an olefinic proton (δ 5.28, *t*, *J* = 3.8 Hz, H-12), a characteristic [6] methine proton at δ 2.43 (*d*, *J* = 10.7 Hz, H-18), four methyls located at quaternary carbons (δ 0.74, 0.95, 1.01 and 1.07, each 3H, *s*) and two methyls on secondary carbons (δ 0.85, *J* = 6.8 and 0.89, *J* = 6.5 Hz, each 3H, *d*). These data along with the characteristic ¹³C NMR chemical shifts of C-12 and C-13 at δ 126.1 and 137.1, respectively [7], suggested that **1** belongs to the $\Delta^{12}\alpha$ -amyrin series of pentacyclic triterpenoids. Compound **1** formed the methyl derivative **1a** (δ OMe 3.57) on reaction with diazomethane confirming the carboxyl function indicated by the IR spectrum. However, it did not form an acetyl derivative on reaction with acetic anhydride–pyridine, indicating the presence of a tertiary hydroxyl group.

The ¹H NMR spectrum further exhibited a three-proton singlet at δ 1.98 indicative of the presence of an acetyl group. A methine proton at δ 5.03 (*t*, *J* = 3.18 Hz, H-22), related to δ 75.6 in the hetero COSY spectrum, and

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an ion at m/z 468.3260 ($\text{C}_{30}\text{H}_{44}\text{O}_4$) in the HR-mass spectrum, resulting from the loss of acetic acid from the molecular ion, supported the acetoxy group in **1**. The characteristic retro-Diels–Alder fragments [8] of **1** at m/z

246.1607 and 285.1901 (see formula 1) indicated the location of the acetoxy group in ring D/E with the carboxylic group at C-17 and the hydroxyl group and the remaining oxygen function in ring A/B. Fragments m/z

69.0694 and 171.1085 located the acetoxy group at C-22. Its β -disposition was evident from the chemical shift and coupling constants of H-22 [9]. Furthermore, the ^1H NMR spectrum showed a pair of double doublets centred at δ 4.20 ($J = 8.45, 2.55$ Hz) and 3.87 ($J = 8.45, 0.5$ Hz) for the two non-equivalent methylene protons of the hemiketal system. This region of the ^1H NMR spectrum showed a close similarity with that of lantanilic acid [9], thus ascribing these signals to H-25a and H-25b which were confirmed from cross peaks in the COSY spectrum. Therefore, the remaining oxygen function was placed in ring A as a part of the hemiketal structure. Since the C (C-25) forming the epoxide linkage with C-3 is β -oriented, the hydroxyl group was given an α -disposition. In the light of these observations, the structure of **1** has been established as 22 β -acetoxy-3,25-epoxy-3 α -hydroxy-12-ursen-28-oic acid, which was substantiated by various fragments in the HR-mass spectrum (see formula **1**) and the ^{13}C NMR spectral data (Table 1).

Camaric acid (**2**) did not show a molecular ion peak (EI-, FD- or FAB-mass spectra) and the molecular formula $\text{C}_{35}\text{H}_{52}\text{O}_6$ was derived through exact measurement

of various mass fragment ions and ^{13}C NMR spectroscopy (broad band, DEPT and heteroCOSY). It showed IR absorption bands at 3500–2600 (CO_2H , OH), 2910, 2850 (CH), 1680–1720 (br C=O of CO_2H and α, β -unsaturated ester) and 1640 cm^{-1} (C=C); while its UV spectrum showed an absorption maximum at 217 nm. It also formed a methyl derivative (**2a**) on reaction with diazomethane, confirming the presence of a CO_2H group in the molecule. The ^1H NMR spectrum exhibited six methyl singlets at δ 0.75, 0.88, 0.95, 0.99, 1.01 and 1.14, two triplets at δ 5.00 (1H, $J = 3.0$ Hz, H-22 α) and 5.36 (1H, $J = 3.75$ Hz, H-12), and two double doublets at δ 4.21 (1H, $J = 8.38, 2.28$ Hz, H-25a) and 3.38 (1H, $J = 8.88, 1.10$ Hz, H-25b). Retro-Diels–Alder fragmentation around ring C followed by the loss of the ester side chain in the form of the acid, resulted in an ion at m/z 246.1628 ($\text{C}_{16}\text{H}_{22}\text{O}_2$). These data showed a close similarity of **2** with lantanilic acid [9], i.e. a β -oriented hemiketal system at C-3 with C-25, a double bond at C-12, a β -oriented ester side chain at C-22 and a carboxyl group at C-17 in the β -amyrin skeleton. Characteristic peaks in the ^{13}C NMR at δ 122.8 (C-12) and 143.1 (C-13) confirmed the $\Delta^{12}\beta$ -amyrin skeleton [10].

That **2** differed from lantanilic acid [9] in the nature of the ester moiety only was obvious from the ^1H NMR spectrum. It showed a three proton quintet at δ 1.78 ($J = 1.52$ Hz, H-5'), a three proton doublet of quartets at δ 1.94 ($J = 7.24, 1.52$ Hz, H-4') and a one proton quartet of quartets at δ 5.97 ($J = 7.24, 1.52$ Hz, H-3') indicating a 2',3'-dimethyl acryloxy function [11]. This was supported by the ^{13}C NMR chemical shifts of the ester carbons (Table 1) and the HR-mass spectral fragments at m/z 468.3246 [$\text{M} - 100$] $^+$ ($\text{C}_{30}\text{H}_{44}\text{O}_4$) and 83.0390 ($\text{C}_5\text{H}_7\text{O}$). It may also be noted that this side chain caused a down field shift of H-18 from *ca* δ 2.8, characteristic of $\Delta^{12}\beta$ -amyrin [6], to δ 3.03 (1H, *dd*, $J = 13.8, 3.7$ Hz). These data led to the structure of **2** as 3,25-epoxy-3 α -hydroxy-22 β (2-methyl-2Z-butenoyloxy)-12-oleanen-28-oic acid.

Oleanolic acid [12], pomolic acid [13], lantanolic acid [14], lantanilic acid [9] and lantic acid [15] were identified through comparison of their spectral data with the published values. This is the first report of the isolation of oleanolic acid and pomolic acid from this plant. However, lantanolic acid, lantanilic acid and lantic acid have been isolated previously from this source. In the present studies ^{13}C NMR assignments of lantanolic acid and lantic acid and complete ^1H and ^{13}C NMR assignments of lantanilic acid have also been made with the help of extensive ^{13}C NMR (broad band and DEPT experiments) and 2D NMR studies including COSY-45, NOESY, *J*-resolved and hetero COSY.

EXPERIMENTAL

Mps: uncorr; MS: Finnigan MAT 112 and 312 double focusing mass spectrometers connected to a PDP 11/34 computer system; NMR (CDCl_3): 300 MHz for ^1H and 75 MHz for ^{13}C . The chemical shifts are reported in δ (ppm) and the coupling constants are in Hz. In the ^{13}C NMR spectra various carbons have been identified

Table 1. ^{13}C NMR spectral data of compounds **1**, **2**, **5**–**7**

C	1	2	5	6	7
1	35.1	34.7	34.7	34.7	35.0
2	27.9	27.8	27.8	27.8	27.8
3	98.9	98.9	98.7	98.9	98.7
4	38.8	38.4	38.5	38.4	38.4
5	50.3	50.4	50.4	50.5	50.3
6	19.5	19.7	19.7	19.8	19.6
7	31.2	31.0	31.0	31.1	31.3
8	40.2	40.3	41.7	40.3	40.2
9	41.9	42.0	41.9	42.1	42.0
10	34.9	35.2	35.1	35.2	34.9
11	23.1	23.8	23.1	23.8	23.7
12	126.1	122.8	122.5	122.6	125.7
13	137.1	143.1	143.6	143.1	138.2
14	42.4	42.0	42.1	42.1	41.8
15	29.6	29.5	28.1	29.5	29.4
16	24.8	24.3	23.7	24.2	24.2
17	51.7	50.8	46.7	50.9	48.1
18	49.3	39.2	41.6	39.3	53.2
19	39.2	45.9	45.7	45.9	39.1
20	38.7	30.1	30.7	30.1	38.8
21	34.9	37.9	33.9	37.8	30.7
22	75.6	76.1	32.3	75.4	36.6
23	27.1	27.3	27.2	27.3	27.2
24	16.8	17.3	17.8	17.4	17.5
25	67.8	67.7	67.7	67.9	67.9
26	18.3	18.3	18.3	18.3	18.3
27	23.0	26.2	25.4	26.3	23.2
28	178.0	178.9	182.5	178.0	182.3
29	17.6	33.7	33.0	33.7	16.9
30	21.1	25.4	23.5	25.4	21.1
1'	170.0	166.5	—	165.4	—
2'	20.7	127.9	—	116.1	—
3'	—	138.2	—	156.8	—
4'	—	15.6	—	27.3	—
5'	—	20.5	—	20.2	—

through BB, DEPT and hetero COSY spectra and comparison with related compounds [7, 9, 11]. VLC and flash CC: silica gel PF₂₅₄ and silica gel E. Merck 9385. 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.

Air-dried aerial parts of *Lantana camara* (10 kg), collected from the Karachi region, were repeatedly extracted with MeOH at room temp. The concd extract, obtained on removal of the solvent from the combined extracts under red. pres., was partitioned between EtOAc and H₂O. The EtOAc phase was treated with 4% aq. soln. of Na₂CO₃ to separate the acidic from the neutral fraction. The EtOAc layer containing the neutral fraction was washed with water, dried (Na₂SO₄) and passed through active C. The charcoal bed was successively washed with EtOAc and MeOH-C₆H₆ (1:1) which were combined on the basis of TLC. The residue obtained on removal of the solvent was divided into petrol-soluble and petrol-insoluble fractions. The petrol-insoluble fraction was again divided into Et₂O-soluble and Et₂O-insoluble portions. The residue (17.5 g), obtained from the Et₂O-soluble portion on removal of the solvent, was subjected to VLC (petrol-EtOAc in order of increasing polarity). On pooling together the fractions on the basis of TLC, nine fractions (1–9) were obtained of which frs 4–6 were obtained in workable quantities and were further sep'd. Fr. 4 (3.5 g), which was eluted with petrol-EtOAc (4:1), was again subjected to VLC (petrol-EtOAc in order of increasing polarity), which ultimately furnished 6 fractions (I–VI). Fr. IV (2.6 g) (petrol-EtOAc, 7:1 eluate) was further subjected to VLC (petrol, petrol-EtOAc, in order of increasing polarity), ultimately furnishing two pure compounds: oleanolic acid (3) (petrol-EtOAc, 9:1 eluate; 128 mg) and camaric acid (2) (EtOAc eluate; 787 mg). Fr. V obtained on elution with petrol-EtOAc (7:1) afforded pure camaric acid (2) (400 mg). Fr. 5 (petrol-EtOAc, 4:1 eluate) of the main VLC, was also rechromatographed (VLC, petrol, petrol-EtOAc, in order of increasing polarity), ultimately yielding three major pure components: oleanolic acid (petrol-EtOAc, 7:1 eluate; 541 mg) (3), pomolic acid (petrol-EtOAc, 7:1 eluate; 95 mg) (4) and lantanilic acid (EtOAc eluate; 2.66 g) (6). Another major fraction (6), on rechromatography by VLC, afforded lantanolic acid (5) (9.6 mg) and lantic acid (7) (67.5 mg) on elution with petrol-EtOAc (3:1) in order of polarity and camarinic acid (1) (116 mg) from the petrol-EtOAc (7:3, 6:4, 1:1) and EtOAc eluates.

Camarinic acid (1). Needles, 116 mg (MeOH, mp. 204–205°). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 210; IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm⁻¹: 3500–2600 (br, OH and CO₂H), 1738–1680 (acid and ester carbonyls) and 1620 (C=C); HR-MS *m/z* (rel. int.): 528.3452 [M]⁺ (C₃₂H₄₈O₆) (2), 468.3260 [M – HOAc]⁺ (C₃₀H₄₄O₄) (12), 450.3107 [468 – H₂O]⁺ (C₃₀H₄₂O₃) (3), 424.3310 [468 – CO₂]⁺ (C₂₉H₄₄O₂) (3), 422.3145 [468 – CO₂H – H]⁺ (C₂₉H₄₂O₂) (3), 372.2308 (C₂₃H₃₂O₄) (4), 354.2222 (C₂₃H₃₀O₃) (8), 285.1901 (C₁₉H₂₅O₂) (24), 246.1607 (C₁₆H₂₂O₂) (5), 241.1964 (C₁₈H₂₅) (20), 201.1625 (C₁₅H₂₁) (12), 185.1265 (C₁₄H₁₇)

(8), 171.1085 (C₉H₁₅O₃) (44), 133.0968 (C₁₀H₁₃) (12), 131.0844 (C₁₀H₁₁) (10), 119.0848 (C₉H₁₁) (16), 105.0700 (C₁₀H₉) (18) and 69.0694 (C₅H₉) (15); ¹H NMR: δ 2.10 (1H, *m*, H-1a), 1.20 (1H, *m*, H-1b), 1.41 (1H, *m*, H-2a), 1.19 (2H, *m*, H-2b and H-5), 1.51 (2H, *m*, H-6), 1.38 (2H, *m*, H-7), 1.69 (1H, *m*, H-9), 2.0 (2H, *m*, H-11), 5.28 (1H, *t*, *J* = 3.8 Hz, H-12), 2.16 (1H, *m*, H-15a), 1.70 (1H, *m*, H-15b), 1.86 (2H, *m*, H-16), 2.43 (1H, *d*, *J* = 10.74 Hz, H-18), 1.32 (1H, *m*, H-19), 0.98 (1H, *m*, H-20), 1.75 (2H, *m*, H-21), 5.03 (1H, *t*, *J* = 3.18 Hz, H-22), 1.01 (3H, *s*, H-23), 0.74 (3H, *s*, H-24), 4.20 (1H, *dd*, *J* = 8.45, 2.55 Hz, H-25a), 3.87 (1H, *dd*, *J* = 8.45, 0.50 Hz, H-25b), 0.95 (3H, *s*, H-26), 1.07 (3H, *s*, H-27), 0.85 (3H, *d*, *J* = 6.75 Hz, H-29), 0.89 (3H, *d*, *J* = 6.62 Hz, H-30) and 1.98 (3H, *s*, H-2').

Methylation of compound 1. To a soln of 1 (10 mg) in MeOH was added an ethereal soln of CH₂N₂ (in excess) and the mixture kept overnight at room temp. Removal of the solvent from the reaction mixture furnished the methyl derivative **1a** as rods (MeOH). HR-MS *m/z* (rel. int.): 542.3601 [M]⁺ (C₃₃H₅₀O₆) (10); ¹H NMR: δ 5.27 (1H, *t*, *J* = 3.79 Hz, H-12), 2.42 (1H, *d*, *J* = 11.00 Hz, H-18), 5.0 (1H, *t*, *J* = 3.17 Hz, H-22 α), 1.01 (3H, *s*, H-23), 0.75 (3H, *s*, H-24), 4.23 (1H, *dd*, *J* = 8.45, 2.55 Hz, H-25a), 3.87 (1H, *dd*, *J* = 8.45, 0.5 Hz, H-25b), 0.94 (3H, *s*, H-26), 1.06 (3H, *s*, H-27), 0.84 (3H, *d*, *J* = 6.72 Hz, H-29), 0.90 (3H, *d*, *J* = 6.60 Hz, H-30), 1.97 (3H, *s*, Ac) and 3.46 (3H, *s*, CO₂Me).

Camaric acid (2). Needles, 787 mg (MeOH, mp. 188–189°). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 217; IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm⁻¹: 3500–2600 (CO₂H, OH), 2910, 2850 (CH), 1680–1720 (br, C=O of CO₂H and α,β -unsaturated ester) and 1640 (C=C); HR-MS *m/z* (rel. int.): 468.3246 [M – 2-methyl-2-butenoic acid]⁺ (C₃₀H₄₄O₄) (88), 450.3136 [468 – H₂O]⁺ (C₃₀H₄₂O₃) (12), 424.3340 [468 – CO₂]⁺ (C₂₉H₄₄O₂) (16), 285.1897 (C₁₉H₂₅O₂) (38), 246.1628 [r.D.A. fragment-acid]⁺ (C₁₆H₂₂O₂) (10), 241.1965 [285 – CO₂]⁺ (C₁₈H₂₅) (42), 203.1763 (C₁₅H₂₃) (28), 201.1626 (C₁₅H₂₁) (22), 133.1004 (C₁₀H₁₃) (32), 131.0858 (C₁₀H₁₁) (18), 119.0863 (C₉H₁₁) (34), 105.0690 (C₈H₉) (24) and 83.0390 (C₅H₇O) (100); ¹H NMR: δ 2.10 (1H, *m*, H-1a), 1.20 (1H, *m*, H-1b), 1.40 (1H, *m*, H-2a), 1.20 (2H, *m*, H-2b and H-5), 1.50 (2H, *m*, H-6), 1.37 (2H, *m*, H-7), 1.70 (1H, *m*, H-9), 2.0 (1H, *m*, H-11a), 1.80 (1H, *m*, H-11b), 5.36 (1H, *t*, *J* = 3.75 Hz, H-12), 2.15 (1H, *m*, H-15a), 1.70 (1H, *m*, H-15), 1.85 (2H, *m*, H-16), 3.03 (1H, *dd*, *J* = 13.8, 3.7 Hz, H-18), 1.73 (1H, *m*, H-19a), 1.27 (1H, *m*, H-19b), 1.75 (1H, *m*, H-21a), 1.50 (1H, *m*, H-21b), 5.0 (1H, *t*, *J* = 3.0 Hz, H-22 α), 1.01 (3H, *s*, H-23), 0.75 (3H, *s*, H-24), 4.21 (1H, *dd*, *J* = 8.38, 2.28 Hz, H-25a), 3.88 (1H, *dd*, *J* = 8.38, 1.10 Hz, H-25b), 0.99 (6H, *s*, H-26 and H-27), 0.88 (3H, *s*, H-29), 1.14 (3H, *s*, H-30), 5.97 (1H, *qq*, *J* = 7.24, 1.52 Hz, H-3'), 1.94 (3H, *dq*, *J* = 7.24, 1.52 Hz, H-4') and 1.78 (3H, *quint*, *J* = 1.52 Hz, H-5').

Methylation of compound 2. Compound 2 (10 mg) was taken up in MeOH and treated with an ethereal soln of CH₂N₂. On keeping the reaction mixture at room temp. overnight and usual work-up afforded the methyl derivative, **2a** as needles (MeOH). HR-MS *m/z* (rel. int.): 482.3392 [M – 2-methyl-2-butenoic acid]⁺ (C₃₁H₄₆O₄) (72); ¹H NMR: δ 5.34 (1H, *t*, *J* = 3.75 Hz, H-12), 3.02 (1H,

dd, J = 13.8, 3.9 Hz, H-18), 5.02 (1H, t, J = 3.01 Hz, H-22 α), 1.01 (3H, s, H-23), 0.74 (3H, s, H-24), 4.21 (1H, dd, J = 8.37, 2.27 Hz, H-25a), 3.87 (1H, dd, J = 8.37, 1.09 Hz, H-25b), 0.98 (6H, s, H-26, H-27), 0.88 (3H, s, H-29), 1.12 (3H, s, H-30), 6.00 (1H, qq, J = 7.22, 1.51 Hz, H-3'), 1.96 (3H, dq, J = 7.22, 1.51 Hz, H-4'), 1.79 (3H, quintet, J = 1.51 Hz, H-5') and 3.44 (3H, s, CO₂Me).

Lantanilic acid (6). ¹H NMR: δ 2.12 (1H, *m*, H-1a), 1.20 (2H, *m*, H-1b and H-5), 1.40 (1H, *m*, H-2a), 1.19 (1H, *m*, H-2b), 1.50 (2H, *m*, H-6), 1.36 (2H, *m*, H-7), 1.70 (1H, *m*, H-9), 2.0 (1H, *m*, H-11a), 1.80 (1H, *m*, H-11b), 5.34 (1H, *t*, *J* = 3.5 Hz, H-12), 2.12 (1H, *m*, H-15a), 1.70 (1H, *m*, H-15b), 1.86 (2H, *m*, H-16), 3.0 (1H, *dd*, *J* = 13.30, 4.00 Hz, H-18), 1.70 (1H, *m*, H-19a), 1.25 (1H, *m*, H-19b), 1.75 (1H, *m*, H-21a), 1.47 (1H, *m*, H-21b), 4.98 (1H, *t*, *J* = 3.25 Hz, H-22 α), 0.99 (3H, *s*, H-23), 0.73 (3H, *s*, H-24), 4.20 (1H, *dd*, *J* = 8.75, 2.29 Hz, H-25a), 3.88 (1H, *d*, *J* = 8.75 Hz, H-25b), 0.93 (3H, *s*, H-26), 0.97 (3H, *s*, H-27), 0.85 (3H, *s*, H-29), 1.10 (3H, *s*, H-30), 5.54 (1H, *br s*, H-2'), 1.82 (3H, *s*, H-4') and 2.10 (3H, *s*, H-5').

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