Noroleanane Triterpenoids from the Aerial Parts of *Lantana camara*

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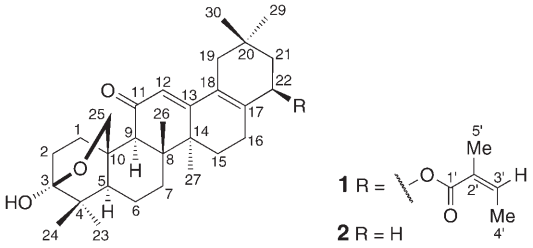
Two novel triterpenoids, lantadienone (**1**) and camaradienone (**2**), were isolated from the aerial parts of *Lantana camara*, along with seven known compounds, lantadene A, lantadene B, β-sitosterol 3-(β-D-glucopyranoside), camaric acid, lantanilic acid, lantanolic acid, and camangeloyl acid. Their structures were elucidated as (3β,22β)-3,25-epoxy-3-hydroxy-22-{[(2*Z*)-2-methyl-1-oxobut-2-enyl]oxy}-28-noroleana-12,17-dien-11-one (**1**) and (3β)-3,25-epoxy-3-hydroxy-28-noroleana-12,17-dien-11-one (**2**), respectively, by means of spectral studies. The triterpenoids **1** and **2** represent 28-noroleananes oxidized at C(11) and C(22) or at C(11), reported for the first time.

Introduction. – *Lantana camara* LINN. (family Verbenaceae) commonly known as lantana, is a hairy shrub, native of tropical America cultivated elsewhere as an ornamental or hedge plant. Different parts of the plant are used for the treatment of various human ailments, such as itches, cuts, ulcers, malaria, influenza, anemia, tumors, swellings, bilious fever, eczema eruptions, rheumatism, stomachache, toothache, scabies, leprosy, and as antiseptic for wounds. The aqueous extract of the leaves showed antihyperglycaemic activity and wound-healing property. 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 [1–4]. Phytochemical studies undertaken by different research groups on different parts of the plant have resulted in the isolation of various terpenoids [3][5], steroids [3], and flavonoids [3][6]. 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 nortriterpenoids, lantadienone (**1**) and camaradienone (**2**), along with seven known compounds, lantadene A (=(22β)-22-{[(2*Z*)-2-methyl-1-oxobut-2-enyl]oxy}-3-oxo-



olean-12-en-28-oic acid) [7], lantadene B (=(22β)-22-[(3-methyl-1-oxobut-2-enyl)-oxy]-3-oxoolean-12-en-28-oic acid) [7], β-sitosterol 3-(β-D-glucopyranoside) (=(3β)-stigmast-5-en-3-ol 3-(β-D-glucopyranoside)) [8], camaric acid (=(3β,22β)-3,25-epoxy-3-hydroxy-22-{[(2*Z*)-2-methyl-1-oxobut-2-enyl]oxy}olean-12-en-28-oic acid) [9], lantanilic acid (=(3β,22β)-3,25-epoxy-3-hydroxy-22-[(3-methyl-1-oxobut-2-enyl)oxy]-olean-12-en-28-oic acid) [10], lantanolic acid (=(3β)-3,25-epoxy-3-hydroxyolean-12-en-28-oic acid) [11], and camangeloyl acid (=(3β,22β)-3,25-epoxy-3-hydroxy-22-{[(2*Z*)-2-methyl-1-oxobut-2-enyl]oxy}-11-oxours-12-en-28-oic acid) [12].

Results and Discussion. – Compound **1** exhibited the molecular-ion peak at *m*/*z* 536 in its EI-MS, the exact mass measurement of which gave its molecular formula as $C_{34}H_{48}O_5$. The IR spectrum showed absorption bands at 3358 (OH), 2928, and 2862 (CH), 1730 (ester C=O), 1653 (conjugated C=O), 1510 (C=C), and 1040 cm^{-1} (C–O), and the UV spectrum exhibited the absorption maxima at 286 and 217 nm. The ^{1}H- and ^{13}C-NMR (*Table 1*), HMBC (*Table 1*), HMQC, ^{1}H,^{1}H-COSY (*Fig. 1*), ^{1}H,^{1}H-TOCSY, NOESY (*Fig. 1*), and MS data (*Fig. 2*), as well as comparison with literature data allowed to establish the structure of lantadienone (**1**) as (3β,22β)-3,25-epoxy-3-hydroxy-22-{[(2*Z*)-2-methyl-1-oxobut-2-enyl]oxy}-28-noroleana-12,17-dien-11-one.

The ^{1}H-NMR spectrum of **1** showed six Me *s* at δ(H) 0.90, 0.91, 0.99, 1.00, 1.04, and 1.14, attributable to six tertiary Me groups, and an olefinic-proton *s* at δ(H) 5.80 (1 H), indicating the presence of the carbonyl group at C(11) of the olean-12-ene type pentacyclic triterpenoid [13]. A pair of broad *d*s at δ(H) 4.76 (J = 8.4 Hz) and 4.18 (J = 8.4 Hz) (δ(C) 66.0 (CH_2)) was attributed to the two nonequivalent CH_2 protons of the 3,25-epoxy moiety. This region of the ^{1}H-NMR spectrum showed a close similarity with that of lantanilic acid and other related compounds [10][12], thus ascribing these signals to H_a–C(25) and H_b–C(25). These assignments were confirmed by cross-peaks in the ^{1}H,^{1}H-COSY (*Fig. 1*), which showed interactions between H_a–C(25) and H_b–C(25) and the interactions of both these protons with H_b–C(1) by a long range coupling (W), as suggested earlier [11] by various authors for this system. A one-proton *t* at δ(H) 5.52 (J = 5.9 Hz; δ(C) 70.7 (CH)) was ascribed to H_α–C(22) indicating the presence of a β-oriented ester side chain (1730 cm^{-1}) at C(22) [9]. The MS of **1** showed a peak at *m*/*z* 83.0491 ($C_5H_7O^+$) and a peak at *m*/*z* 436.2971 ($C_{29}H_{40}O_3^+$), resulting from the loss of 100 mass units from the molecular ion (*Fig. 2*). These observations indicated the presence of a methylbutenoic acid ester side chain at C(22). The signals at δ(H) 6.07 (*qq*, J = 7.2, 1.5 Hz, H–C(3′)), 1.99 (*dq*, J = 7.2, 1.5 Hz, Me(4′)), and 1.87 (*quint.*, J = 1.5 Hz, Me(5′)) and the ^{13}C-NMR, HMQC, and HMBC data (*cf. Table 1*) indicated the presence of a 2-methylbut-2-enoic acid ester side chain with (*Z*)-configuration [14] which was further confirmed by the NOESY interaction H–C(3′) (δ(H) 6.07)/Me(5′) (δ(H) 1.87) (*Fig. 1*). The position of the ester moiety at C(22) was confirmed by observing the HMBC cross-peaks H_α–C(22)/C(16), C(17), C(18), C(21), and C(1′), while the configuration of this ester side chain was established as β on the basis of the NOESY interaction H–C(22)/Me(29). The UV spectrum (286 nm) and the IR spectrum (1653 cm^{-1}) established the presence of an α,β-unsaturated ketone with extended conjugation [15][16]. The position of this ketone moiety at C(11) was further confirmed by a downfield shift of H_a–C(1) (δ(H) 2.92) which is comparable to such a shift in other 11-keto compounds [13][17]. The ^{13}C-NMR signals at δ(C) 122.1 (C(12)), 157.7 (C(13)), 138.5 (C(17)), and 129.4 (C(18)) of a trisubstituted and of a tetrasubstituted C=C bond, along with the UV maximum for extended conjugation (heteroannular), suggested the presence of a 12,17-dien-11-one system in a 28-nortriterpenoidal skeleton. This was supported by the absence of H–C(18) (δ(H) *ca.* 2.8) in the ^{1}H-NMR spectrum [9], by a mass fragment at *m*/*z* 214.1372 ($C_{15}H_{18}O^+$) resulting from the *retro-Diels–Alder* fragment around ring C, followed by the loss of a side chain in the form of angelic acid (=(2*Z*)-2-methylbut-2-enoic acid), and by the HMBC cross-peaks H–C(9)/C(8), C(10), C(11), C(25), and C(26) and H–C(12)/C(9), C(13), C(14), and

Table 1. *^{1}H- and ^{13}C-NMR Data* ($CDCl_3$) *of* **1** *and Corresponding HMBC Correlations.* δ in ppm, J in Hz. Assignments are based on ^{1}H-,^{13}C-NMR (broad-band decoupled, DEPT), ^{1}H,^{1}H-COSY, ^{1}H,^{1}H-TOCSY, NOESY, *J*-resolved, HMQC, and HMBC experiments.

	δ(H)	δ(C)	HMBC (H → C)
CH_2(1)	2.90–2.93 (*m*, H_a), 1.15–1.17 (*m*, H_b)	34.9	C(2), C(3), C(5), C(9), C(10), C(25)
CH_2(2)	2.11–2.14 (*m*, H_a), 1.75–1.78 (*m*, H_b)	29.7	C(3)
C(3)	–	97.6	–
C(4)	–	40.6	–
H–C(5)	1.19–1.21 (*m*)	51.4	–
CH_2(6)	1.53–1.56 (*m*, H_a), 1.50–1.52 (*m*, H_b)	19.1	–
H_a–C(7)	1.57–1.61 (*m*)	31.8	C(5), C(9)
H_b–C(7)	1.50–1.52 (*m*)		–
C(8)	–	42.4	–
H–C(9)	2.54 (*s*)	54.9	C(8), C(10), C(11), C(25), C(26)
C(10)	–	35.1	–
C(11)	–	199.1	–
H–C(12)	5.80 (*s*)	122.1	C(9), C(13), C(14), C(18)
C(13)	–	157.7	–
C(14)	–	41.8	–
H_a–C(15)	1.68–1.71 (*m*)	26.3	C(14), C(16), C(27)
H_b–C(15)	1.53–1.56 (*m*)		C(13), C(14), C(16), C(17), C(27)
CH_2(16)	2.35–2.37 (*m*, H_a), 2.02–2.04 (*m*, H_b)	23.1	–
C(17)	–	138.5	–
C(18)	–	129.4	–
H_a–C(19)	2.11–2.14 (*m*)	39.1	C(13)
H_b–C(19)	1.79–1.82 (*m*)		C(13), C(17), C(18)
C(20)	–	30.2	–
H_a–C(21)	1.84–1.86 (*m*, H_a)	41.0	C(17), C(19), C(20), C(22)
H_b–C(21)	1.53–1.56 (*m*, H_b)		C(17), C(19), C(20), C(22), C(30)
H–C(22)	5.52 (*t*, J = 5.9)	70.7	C(16), C(17), C(18), C(21), C(1′)
Me(23)	1.04 (*s*)	27.4	C(3), C(4), C(5), C(24)
Me(24)	0.99 (*s*)	18.4	C(3), C(4), C(5), C(23)
H_a–C(25)	4.76 (br. *d*, J = 8.4)	66.0	C(3), C(5), C(10)
H_b–C(25)	4.18 (br. *d*, J = 8.4)		C(5), C(10)
Me(26)	0.90 (*s*)	18.0	C(7), C(8), C(9), C(14)
Me(27)	1.14 (*s*)	18.0	C(8), C(13), C(14), C(15)
Me(29)	0.91 (*s*)	27.2	C(19), C(20), C(21), C(30)
Me(30)	1.00 (*s*)	30.4	C(19), C(20), C(21), C(29)
C(1′)	–	167.6	–
C(2′)	–	127.7	–
H–C(3′)	6.07 (*qq*, J = 7.2, 1.5)	138.4	C(5′)
Me(4′)	1.99 (*dq*, J = 7.2, 1.5)	15.8	C(2′), C(3′)
Me(5′)	1.87 (*quint.*, J = 1.5)	20.6	C(1′), C(2′), C(3′)

C(18). This extended conjugation caused an upfield shift of C(12) (δ(C) 122.1), C(13) (δ(C) 157.7), and C(19) (δ(C) 39.1) in the ^{13}C-NMR spectrum as compared to compounds having only an α,β-unsaturated ketone moiety at C(11) [12]. The remaining O-atom was placed at C(3) as an α-oriented OH group as there was no further C*H*–OH proton in the ^{1}H-NMR spectrum, and the β-configuration was attributed to the 3,25-epoxy moiety. A quaternary C-atom signal at δ(C) 97.6 (C(3)) and the HMBC interaction of C(3) with H_a–C(1), H_a–C(2), H_b–C(2), H_a–C(25), H–C(23), and H–C(24) confirmed this hemiketal functionality in ring A.

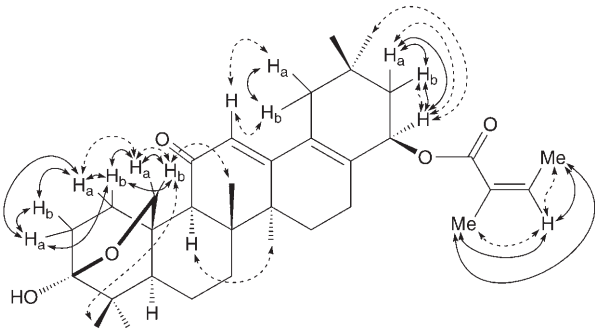


Fig. 1. *Significant ^{1}H,^{1}H-COSY* (↔) *and NOESY* (←– – –→) *interactions of* **1**

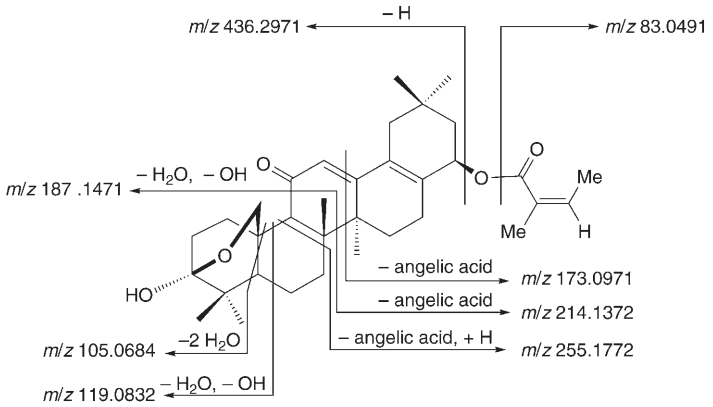


Fig. 2. *Diagnostic EI-MS fragment ions of* **1**

Compound **2** displayed the molecular-ion peak M^+ at *m/z* 438.3142 in the HR-EI-MS consistent with the molecular formula $C_{29}H_{42}O_3$. The IR spectrum exhibited absorption bands at 3357 (OH), 2938, 2859 (CH), 1653 (conjugated C=O), 1520 (C=C), and 1050 cm^{-1} (C–O). The UV spectrum showed strong absorption at 286 nm. The ^{1}H- and ^{13}C-NMR (*Table 2*), HMBC (*Table 2*), HMQC, ^{1}H,^{1}H-COSY (*Fig. 3*), ^{1}H,^{1}H-TOCSY, NOESY (*Fig. 3*), and MS data (*Fig. 4*), as well as comparison with the data of **1**, established the structure of camaradienone (**2**) as (3β)-3,25-epoxy-3-hydroxy-28-noroleana-12,17-dien-11-one.

In the ^{1}H-NMR spectrum of **1**, the presence of six sharp *s* at δ(H) 0.87, 0.88, 0.90, 0.99, 1.03, and 1.13 for six tertiary Me groups and the NMR signals for H–C(12), C(11), C(12), C(13), C(17), and C(18) described below suggested that **2** is also a 28-nortriterpenoid of the oleanane type. The ^{1}H-NMR spectrum exhibited a pair of broad *d*s at δ(H) 4.75 (J = 8.4 Hz) and 4.17 (J = 8.4 Hz) for the two nonequivalent CH_2 protons of the 3,25 epoxy moiety. This region of the ^{1}H-NMR spectrum showed a close similarity with that of **1**. Thus these signals were assigned to H_a–C(25) and H_b–C(25), and the assignment was confirmed by cross-peaks in the ^{1}H,^{1}H-COSY (*Fig. 3*) which showed interactions between H_a–C(25) and H_b–C(25) and the interactions of both these protons with H_b–C(1), as observed for **1**. A *s* for an olefinic proton (δ(H) 5.71) in the ^{1}H-NMR spectrum and signals at δ(C) 199.1 (C(11)),

Table 2. *^{1}H- and ^{13}C-NMR Data* ($CDCl_3$) *of* **2** *and Corresponding HMBC Correlations.* δ in ppm, *J* in Hz. Assignments are based on ^{1}H-,^{13}C-NMR (broad-band decoupled, DEPT), ^{1}H,^{1}H-COSY, ^{1}H,^{1}H-TOCSY, NOESY, *J*-resolved, HMQC and HMBC experiments.

	δ(H)	δ(C)	HMBC (H → C)
H_a–C(1)	2.95–2.98 (*m*)	35.0	C(2), C(3), C(5), C(10), C(25)
H_b–C(1)	1.15–1.18 (*m*)		–
H_a–C(2)	2.11–2.14 (*m*)	29.8	C(1), C(3), C(10)
H_b–C(2)	1.75–1.78 (*m*)		C(1), C(3), C(10)
C(3)	–	97.7	–
C(4)	–	40.6	–
H–C(5)	1.19–1.22 (*m*)	51.4	–
CH_2(6)	1.57–1.60 (*m*, H_a), 1.49–1.52 (*m*, H_b)	19.1	–
CH_2(7)	1.57–1.60 (*m*, H_a), 1.49–1.52 (*m*, H_b)	31.8	–
C(8)	–	42.4	–
H–C(9)	2.54 (*s*)	54.9	C(1), C(8), C(10), C(11), C(25), C(26)
C(10)	–	35.2	–
C(11)	–	199.1	–
H–C(12)	5.71 (*s*)	119.7	C(9), C(14), C(18)
C(13)	–	158.9	–
C(14)	–	42.2	–
H_a–C(15)	1.70–1.73 (*m*)	26.5	–
H_b–C(15)	1.49–1.52 (*m*)		C(13), C(14), C(16), C(17), C(27)
CH_2(16)	2.21–2.24 (*m*, H_a), 2.04–2.07 (*m*, H_b)	28.5	–
C(17)	–	142.1	–
C(18)	–	125.4	–
H_a–C(19)	1.94–1.98 (*m*)	39.0	–
H_b–C(19)	1.70–1.73 (*m*)		C(18), C(20)
C(20)	–	29.2	–
H_a–C(21)	1.94–1.98 (*m*)	34.5	–
H_b–C(21)	1.31–1.33 (*m*)		C(17), C(19), C(20), C(29), C(30)
H_a–C(22)	2.11–2.14 (*m*)	29.9	C(17), C(18), C(20), C(21)
H_b–C(22)	1.70–1.73 (*m*)		–
Me(23)	1.03 (*s*)	27.4	C(3), C(4), C(5), C(24)
Me(24)	0.99 (*s*)	18.4	C(3), C(4), C(5), C(23)
H_a–C(25)	4.75 (br. *d*, *J* = 8.4)	66.1	C(3), C(5), C(10)
H_b–C(25)	4.17 (br. *d*, *J* = 8.4)		C(10)
Me(26)	0.90 (*s*)	18.0	C(7), C(8), C(9), C(14)
Me(27)	1.13 (*s*)	18.2	C(13), C(14), C(15)
Me(29)	0.87[a]) (*s*)	28.4[a])	C(19), C(20), C(21), C(30)
Me(30)	0.88[a]) (*s*)	28.2[a])	C(19), C(20), C(21), C(29)

[a]) δ(H) or δ(C) values may be interchanged.

119.7 (C(12)), 158.9 (C(13)), 142.1 (C(17)), and 125.4 (C(18)) in the ^{13}C-NMR spectrum, along with the IR and UV data, supported a 12,17-dien-11-one system in the 28-noroleanane skeleton, as observed in **1**. This (heteroannular) dienone system in rings C and D was confirmed by the absence of H–C(18) (δ(H) *ca.* 2.8) in the ^{1}H-NMR spectrum and the presence of a *retro-Diels–Alder* fragment at *m*/*z* 216.1514 ($C_{15}H_{20}O^+$) in the HR-EI-MS (*Fig. 4*). The remaining O-atom in **2** was placed at C(3) as α-oriented OH group due to the β-configuration of 3,25-epoxy moiety. A quaternary C-atom at δ(C) 97.7 was assigned to C(3). This hemiketal moiety was confirmed by observing interactions of H_a–C(1), H_a–C(2), H_b–C(2), H_a–C(25), H–C(23), and H–C(24) with C(3) in the HMBC plot (*Table 2*).

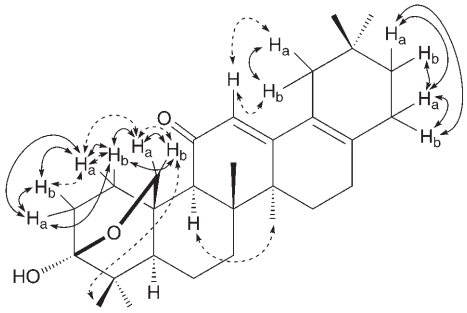


Fig. 3. *Significant $^1H,^1H$-COSY* (↔) *and NOESY* (←– – –→) *interactions of* **2**

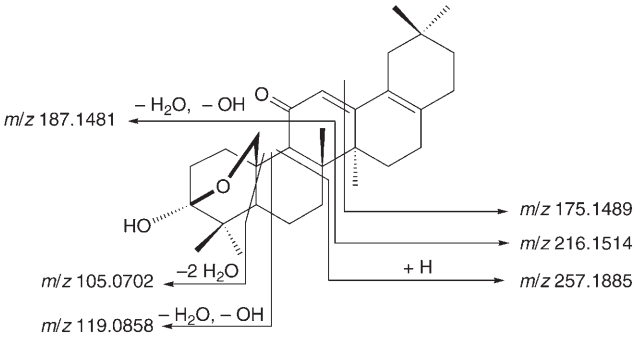
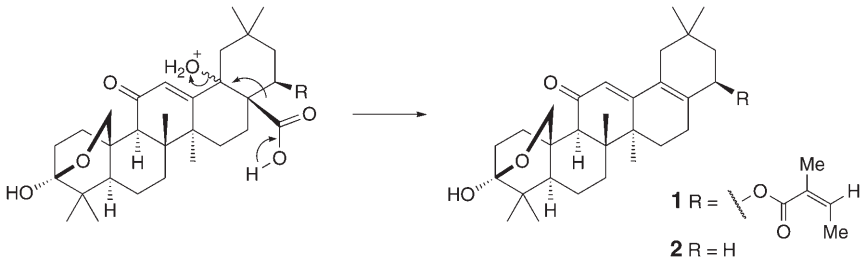


Fig. 4. *Diagnostic EI-MS fragment ions of* **2**

Compounds **1** and **2** are the first examples of a 28-noroleana-12,17-diene-type triterpenoid with both the C(11) and C(22) positions or the C(11) position oxygenated. They probably arise through a decarboxylative removal of the OH group from 18-hydroxyolean-12-en-28-carboxylic acid derivatives. A plausible biosynthetic route is shown in the *Scheme*.

Scheme. *Plausible Biogenetic Pathway for Compounds* **1** *and* **2**



It is important to note that this is the first report of the isolation of 28-nortriterpenoids from the genus *Lantana*.

Experimental Part

General. Vacuum liquid chromatography (VLC): silica gel *60PF$_{254}$* (*Merck*). Flash column chromatography (FC): *Eyela-Flash-Column-EF-10* chromatograph; silica gel *9385* (*Merck*; 0.040–0.063 mm). Prep. TLC: silica gel *60PF$_{254}$* (*Merck*). Anal. TLC: *Merck silica gel Si F$_{254}$* precoated aluminium foils (0.2 mm thickness); detection by spraying with I_2. HPLC: *JAI-LC-908W* instrument; *SIL-10-A-06* column, flow rate 4 ml/min; *S-310A* UV/VIS (detection wavelength 254 nm) and differential refractometer *RI-5* detectors. UV Spectra: *Hitachi-U-3200* spectrophotometer; λ_{max} in nm. IR Spectra: *Jasco-A-302* spectrophotometer; $\tilde{\nu}_{max}$ in cm^{-1}. NMR Spectra: *Bruker* spectrometers; ^1H, COSY, NOESY, TOCSY, and *J*-resolved at 300 and 500 MHz; ^{13}C at 75 and 125 MHz; chemical shifts δ in ppm rel. to Me_4Si as internal standard, coupling constants *J* in Hz. MS: *Finnigan-MAT-311A* (EI; 70 eV) and *Jeol-JMS-HX-110* mass spectrometer (HR-EI; 70 eV); sources at 250°; *m/z* (rel. %).

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) collected from the Karachi region were repeatedly extracted with MeOH at r.t. The concentrated extract, obtained on evaporation of the solvent from the combined extracts possessing nematicidal activity, was partitioned between AcOEt and H_2O. The AcOEt phase was treated with 4% aq. Na_2CO_3 soln. to separate the acidic from the neutral fraction. The AcOEt layer containing the neutral fraction was washed with H_2O, dried (Na_2SO_4), and passed through activated charcoal. The charcoal bed was successively washed with AcOEt and MeOH/benzene 1:1, and the fractions were combined on the basis of TLC. The residue obtained after evaporation of the solvent from the AcOEt layer and washings was divided into petroleum ether soluble and petroleum ether insoluble fractions. The petroleum ether insoluble fraction was further divided into Et_2O-soluble and Et_2O-insoluble fractions. The Et_2O-insoluble fraction was again divided into AcOEt-soluble and AcOEt-insoluble portions. The AcOEt-soluble fraction (40 g) was subjected to VLC ($CHCl_3$ and $CHCl_3$/MeOH of increasing polarity), which ultimately furnished *Fractions 1–9* on combining the eluates on the basis of TLC.

Fr. 1 (26.0 g; $CHCl_3$ and $CHCl_3$/MeOH 9.9:0.1 eluates) was further subjected to VLC (petroleum ether and petroleum ether/AcOEt of increasing polarity) which ultimately furnished *Fr. 1.1–1.8* on combining the eluates on the basis of TLC. *Fr. 1.3* (5.6 g) obtained on elution with petroleum ether/AcOEt 8:2 and 7:3 was subjected to FC ($CHCl_3$/MeOH of increasing polarity), which furnished three pure compounds *camaric acid* (5.0 mg; $CHCl_3$/MeOH 9.8:0.2 eluate), *lantanilic acid* (4.0 mg; $CHCl_3$/MeOH 9.8:0.2 eluate), and *lantanolic acid* (6.0 mg; $CHCl_3$/MeOH 9.8:0.2 eluate), along with two major fractions, *Fr. 1.3.4* ($CHCl_3$/MeOH 9.7:0.3 eluate) and *Fr. 1.3.5* ($CHCl_3$/MeOH 9.7:0.3 eluate), in order of polarity. These fractions were purified by prep. recycling HPLC (*SIL-10-A-06*, isocratic $CHCl_3$/^{i}PrOH 9.6:0.4, flow rate 4 ml/min). *Fr. 1.3.4* afforded *lantadienone* (**1**; 4.0 mg; t_R 12 min) and *camangeloyl acid* (18.0 mg; t_R 40 min), while *Fr. 1.3.5* gave *camaradienone* (**2**; 2.0 mg; t_R 15 min).

In another workup procedure, the petroleum ether insoluble fraction was subjected to VLC (petroleum ether and petroleum ether/AcOEt of increasing polarity): *Fr. 10–24. Fr. 12* (1.4 g; petroleum ether/AcOEt 9:1 and 8:2 eluates) was subjected to FC (petroleum ether and petroleum ether/AcOEt of increasing polarity): *Fr. 12.1–12.24. Fr. 12.17* (petroleum ether/AcOEt 8:2 eluate) gave two major spots on TLC which were separated on TLC foils ($CHCl_3$/MeOH 9.8:0.2; 2 times): *lantadene A* (5.0 mg) and *lantadene B* (3.0 mg). The residue obtained from *Fr. 15* (petroleum ether/AcOEt 2:8, 1:9, and 100% AcOEt eluates), after standing in $CHCl_3$/MeOH 1:1 overnight at r.t. and recrystallization from the same solvent, afforded *β-sitosterol 3-(β-*D*-glucopyranoside)* (6.0 mg) as colorless flowers of needles.

Lantadienone (*=(3β,22β)-3,25-Epoxy-3-hydroxy-22-{[(2Z)-2-methyl-1-oxobut-2-enyl]oxy}-28-noroleana-12,17-dien-11-one*; **1**): Amorphous powder. UV (MeOH): 217, 286. IR ($CHCl_3$): 3358, 2928, 2862, 1730, 1653, 1510, 1458, 1385, 1040. ^1H- (500 MHz) and ^{13}C-NMR (125 MHz): *Table 1*. EI-MS: 536 (5, M^+), 518 (17), 436 (37), 418 (11), 403 (6), 255 (11), 214 (3), 187 (13). 171 (18), 133 (9), 119 (16), 105 (18), 83 (88), 55 (100). HR-EI-MS: 536.3555 (M^+, $C_{34}H_{48}O_5^+$; calc. 536.3502).

Camaradienone (*=(3β)-3,25-Epoxy-3-hydroxy-28-noroleana-12,17-dien-11-one*; **2**): Amorphous powder. UV (MeOH): 286. IR ($CHCl_3$): 3357, 2938, 2859, 1653, 1520, 1458, 1382, 1050. ^1H-

(500 MHz) and ^{13}C-NMR (125 MHz): *Table 2*. EI-MS: 438 (46, M^+), 423 (32), 420 (17), 257 (58), 216 (28), 187 (10), 173 (20), 133 (14), 119 (21), 105 (41). HR-EI-MS: 438.3142 (M^+, $C_{29}H_{42}O_3^+$; calc. 438.3134).

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Received October 4, 2007