Triterpenoidal Secondary Metabolites from *Lantana Camara* LINN.

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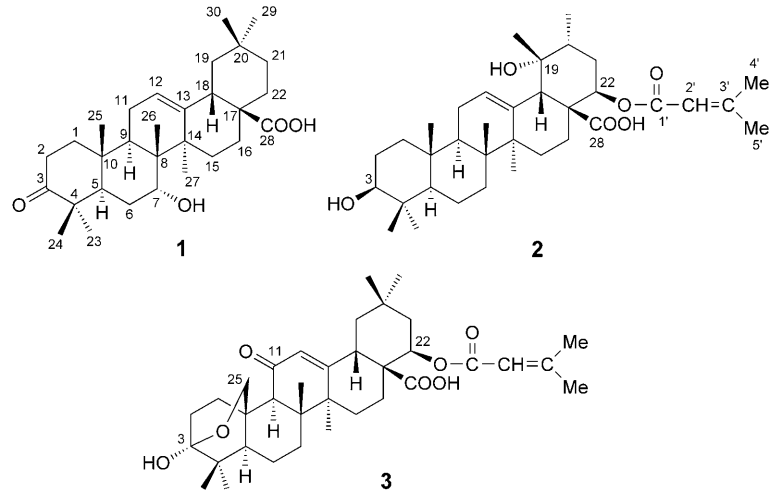
Three new pentacyclic triterpenoids, camarin (**1**), lantacin (**2**), and camarinin (**3**) were isolated from the aerial parts of *Lantana camara* LINN., together with seven known compounds. The structures of the new constituents were elucidated by chemical transformation, HR-EI mass spectrometry, and NMR spectroscopy, including 1D (^{1}H- and ^{13}C-NMR) and 2D (^{1}H,^{1}H-COSY, NOESY, ^{1}H,^{1}H-TOCSY, *J*-resolved, HMQC, and HMBC) experiments.

Introduction. – *Lantana camara* LINN. (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 research groups have resulted in the isolation of various terpenoids, steroids, and flavonoids [3–5].

In the course of our investigations on the constituents of the aerial parts of *L. camara*, we herein report the three new pentacyclic triterpenoids camarin (=(7α)-7-hydroxy-3-oxoolean-12-en-28-oic acid; **1**), lantacin (=(3β,19α,22β)-3,19-dihydroxy-22-[(3-methylbut-2-enoyl)oxy]urs-12-en-28-oic acid; **2**), and camarinin (=(22β)-3β,25-epoxy-3-hydroxy-22-[(3-methylbut-2-enoyl)oxy]-11-oxoolean-12-en-28-oic acid; **3**). Their structures were elucidated on the basis of various 2D-NMR techniques, including ^{1}H,^{1}H-COSY, NOESY, TOCSY, HMQC, and HMBC spectroscopy. In addition, seven known compounds were identified: oleanolic acid [6], ursolic acid [7], pomolic acid [8], lantanolic acid [9], camangeloyl acid [10], lantaninilic acid [11], and lantoic acid [12].

Results and Discussion. – Compound **1** did not show the molecular ion peak in EI-, HR-EI-, and FAB-MS experiments. The molecular formula, $C_{30}H_{46}O_4$, was, thus, established through in-depth analysis of various mass fragment ions (*Fig. 1*) and ^{13}C-NMR (DEPT) data (*Table 1*). The IR spectrum of **1** showed absorption bands at 3420–2610 (br., OH, COOH), 2920 and 2850 (CH), and 1700 cm^{-1} (acid and ketone C=O). The UV spectrum showed an absorption at 206 nm, indicating the lack of conjugation in the molecule. The ^{1}H-NMR spectrum of **1** (*Table 1*) showed seven Me *singlet*s at δ(H) 0.84, 0.90, 0.92, 1.03, 1.06, 1.07, and 1.38. It also displayed resonances for an olefinic H-atom at δ(H) 5.30 (*t*, *J*=3.5 Hz, H–C(12)) and a H-atom at 2.82 (*dd*, *J*=13.8, 4.4 Hz) assigned to H–C(18). These data, along with the characteristic ^{13}C-NMR chemical shifts of C(12) (δ(C) 122.2) and C(13) (143.6) (*Table 1*) [13] suggested that **1** belongs to the Δ^{12}-β-amyrin series of pentacyclic triterpenoids.



Based on the IR signal at 1700 cm^{-1} and the ^{13}C-NMR resonance at δ(C) 217.5, one C=O group was placed at C(3), on biogenetic grounds, as corroborated by downfield NMR signals at δ(H) 2.57–2.63 (*m*, H_a–C(2)) and 2.32–2.38 (*m*, H_b–C(2)), as well as based on HMBC connectivities of the C=O ^{13}C-NMR resonance with CH_2(2), Me(23), and Me(24) (*Table 1*).

Compound **1** formed the corresponding methyl ester [δ(H) 3.64 (*s*, COOMe)] on reaction with CH_2N_2, indicating the presence of a COOH group, as supported by the IR data (broad signal at 3420–2610 cm^{-1}). Similar ^{13}C-NMR data for rings *D* and *E* of related compounds with a COOH group at C(17), as well as characteristic *retro-Diels–Alder* MS fragments [14] of **1** at *m/z* 248.1794, 203.1786, and 133.1011 (*Fig. 1*), indicated the location of the COOH group at C(17), the remaining oxygen function being located in ring *A* or *B*. Furthermore, the ^{1}H-NMR spectrum exhibited a CH signal at δ(H) 4.24–4.32 (*m*, $w_{\frac{1}{2}}$ = 7.0 Hz) correlated to δ(C) 65.9 (CH) in the HMQC spectrum, and exhibited HMBC interactions with C(6), C(8), and C(9). Thus, one axial OH group was placed at C(7), as supported by significant mass fragments at *m/z* 221 ($[C_{14}H_{21}O_2]^+$) in the HR-EI mass spectrum (*Fig. 1*). Its α-configuration was confirmed by NOE interactions of H_β–C(7) with Me(24), Me(25), and Me(26). The presence of the 7α-OH group was further confirmed by a downfield shift of *ca.* 0.30 ppm for Me(27) in the ^{1}H-NMR spectrum due to a 1,3-diaxial interaction [15]. In the light of the above data, the structure of camarin (**1**) was elucidated as (7α)-7-hydroxy-3-oxo-olean-12-en-28-oic acid.

Compound **2** had the molecular formula $C_{35}H_{54}O_6$, as determined by HR-EI-MS and ^{13}C-NMR. Its IR spectrum showed absorption bands at 3428–2650 (br., OH, COOH), 2920 and 2855 (CH), 1730 (ester C=O), 1710 (acid C=O), 1620 (C=C), and 1150 cm^{-1} (C–O). The UV spectrum showed an absorption maximum at 217 nm. Compound **2** also formed a Me ester [δ(H) 3.60 (*s*, COOMe)] upon reaction with CH_2N_2, indicating the presence of a COOH group. The ^{1}H-NMR spectrum of **2** (*Table 2*) showed six Me *singlet*s at δ(H) 0.76, 0.77, 0.96, 0.99, 1.22, and 1.25, one Me *doublet* at δ(H) 0.94 (J = 6.0 Hz), an olefinic H-atom [δ(H) 5.31 (*t*, J = 3.4 Hz, H–

Table 1. *^{1}H- and ^{13}C-NMR Data of Camarin* (**1**). At 400/100 MHz, resp., in $CDCl_3$; δ in ppm, J in Hz.

	δ(H)	δ(C)	HMBC (H→C)
H_a–C(1)	1.87–1.92 (*m*)	39.0	C(3)
H_b–C(1)	1.44–1.49 (*m*)		C(3), C(5)
H_a–C(2)	2.57–2.63 (*m*)	34.1	C(3), C(5)
H_b–C(2)	2.32–2.38 (*m*)		C(3)
C(3)		217.5	
C(4)		37.8	
H_α–C(5)	1.26–1.32 (*m*)	55.3	C(4), C(7), C(10)
H_a–C(6)	2.07–2.13 (*m*)	27.7	
H_b–C(6)	1.70–1.78 (*m*)		
H_β–C(7)	4.24–4.32 (*m*, $w_{\frac{1}{2}}$=7.0)	65.9	C(6), C(8), C(9)
C(8)		37.8	
H_α–C(9)	1.59–1.65 (*m*)	47.2	C(1), C(25), C(26)
C(10)		37.0	
H_a–C(11)	1.91–2.10 (*m*)	23.3	C(10), C(12), C(13)
H_b–C(11)	1.91–2.10 (*m*)		C(10), C(12), C(13)
H–C(12)	5.30 (*t*, *J*=3.5)	122.2	C(9), C(14), C(18)
C(13)		143.6	
C(14)		41.7	
H_a–C(15)	1.58–1.67 (*m*)	28.0	
H_b–C(15)	1.02–1.08 (*m*)		
H_a–C(16)	1.91–2.10 (*m*)	23.6	C(13), C(17), C(28)
H_b–C(16)	1.60–1.67 (*m*)		C(17), C(18), C(22)
C(17)		46.5	
H_β–C(18)	2.82 (*dd*, *J*=13.8, 4.4)	41.2	C(12), C(13)
H_a–C(19)	1.58–1.67 (*m*)	46.0	C(13), C(18) , C(20), C(30)
H_b–C(19)	1.11–1.19 (*m*)	–	C(13), C(18)
C(20)		30.7	
H_a–C(21)	1.32–1.36 (*m*)	33.9	
H_b–C(21)	1.18–1.24 (*m*)	–	
H_a–C(22)	1.69–1.76 (*m*)	32.0	C(16), C(17), C(21), C(28)
H_b–C(22)	1.48–1.57 (*m*)		C(16)
Me(23)	1.07 (*s*)	26.4	C(3), C(5), C(24)
Me(24)	1.03 (*s*)	21.5	C(3), C(4), C(5), C(23)
Me(25)	1.06 (*s*)	15.0	C(1), C(5), C(9), C(10)
Me(26)	0.84 (*s*)	17.0	C(7), C(8), C(9), C(14)
Me(27)	1.38 (*s*)	26.4	C(8), C(13), C(14), C(15)
C(28)		182.0	
Me(29)	0.90 (*s*)	33.0	C(19), C(20), C(21), C(30)
Me(30)	0.92 (*s*)	23.6	C(19), C(20),C(21), C(29)

C(12)], and a broad *singlet* at δ(H) 2.86 (H_β–C(18)), in accord with a 19-substituted Δ^{12}-ursane skeleton. The characteristic ^{13}C-NMR chemical shifts for C(12) (δ(C) 129.0), C(13) (138.0), and C(19) (73.1) [16], and the downfield shift for Me(29), further suggested an OH substituent at C(19). Moreover, the relative downfield shift of H–C(18) at δ(H) 2.86 instead of *ca.* 2.50 [17][18] was indicative of a β-substituted ester group at C(22) (*vide infra*). The ^{1}H-NMR spectrum further indicated a hydroxylated CH [δ(H) 3.24 (*dd*, *J*=10.9, 4.9 Hz); δ(C) 79.0], which was placed at C(3) on biogenetic

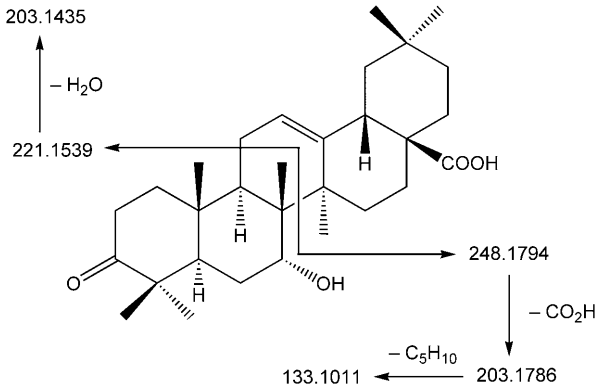


Fig. 1. *Key mass fragmentation of* **1** (in *m/z*)

grounds, and supported by *retro-Diels–Alder* MS fragments at *m/z* 207.1749 and 189.1563 (*Fig. 2*), as well as by HMBC interactions of H–C(3) with C(2), C(4), C(5), C(23), and C(24) (*Table 2*). The 3-OH group was in β-orientation, based on the NMR chemical shifts and coupling constants for H_α–C(3) [19]. Further, the ^{1}H-NMR spectrum indicated a senecioyl[1]) function [δ(H) 5.55 (*s*, H–C(2′); 1.82, 2.12 (2*s*, Me(4′), Me(5′)][10], as supported by the corresponding ^{13}C-NMR chemical shifts of the ester moiety (*Table 2*) and the HR-EI-MS fragments at *m/z* 470.3378 ($C_{30}H_{46}O_4^+$, $[M-100]^+$) and 83.0484 ($C_5H_7O^+$).

The MS fragment ion at *m/z* 262.1584 (*Fig. 2*), resulting from *retro-Diels–Alder* fragmentation and loss of the senecioyl group, supported the presence of the ester moiety either in ring *D* or *E*. The ester was finally placed at C(22), with β-orientation, based on the appearance of a *triplet* at δ(H) 5.03 ($J=3.2$ Hz, 1 H), a CH signal at δ(C) 76.2 in the ^{13}C-NMR (DEPT) spectrum [17], and their mutual HMQC connectivity. The connectivities of H_α–C(22) with C(16), C(17), C(18), C(20), and C(1′) in the HMBC plot confirmed this assignment. From the above data, the structure of lantacin (**2**) was derived as (3β,19α,22β)-3,19-dihydroxy-22-[(3-methylbut-2-enoyl)oxy]urs-12-en-28-oic acid.

Compound **3** showed the M^+ signal at *m/z* 582 in its EI mass spectrum (HR-EI-MS: *m/z* 582.3546), which indicated the molecular formula $C_{35}H_{50}O_7$. Its IR spectrum showed absorption bands at 3450–2650 (br., OH, COOH), 2941 and 2852 (CH), 1730 (ester C=O), 1700 (acid C=O), 1690 (α,β-unsaturated ketone), and 1620 cm^{-1} (C=C). The UV spectrum showed absorption maxima at 248 and 218 nm. The ^{1}H-NMR spectrum (*Table 3*) showed six Me *singlet*s at δ(H) 0.76, 0.90, 0.92, 1.00, 1.11, and 1.37, and a double *doublet* at δ(H) 3.16 ($J=14.1$, 4.2 Hz, 1 H) characteristic of H–C(18) of Δ^{12}-unsaturated oleane triterpenoids [17]. A β-oriented hemiacetal system [10] at C(3), linked *via* an ether O-atom to C(25), was indicated by the following NMR resonances: δ(H) 4.50 (*dd*, $J=8.4$, 2.7, H_a–C(25)) and 4.02 (*dd*, $J=8.4$, 1.1 Hz, H_b–C(25)); δ(C) 65.7 (C(25)). Interaction between H_a–C(25) and H_b–C(25), and long-

[1]) Senecioic acid = 3,3-dimethylprop-2-enoic acid.

Table 2. *^{1}H- and ^{13}C-NMR Data of Lantacin* (**2**). At 400/100 MHz, resp., in $CDCl_3$; δ in ppm, J in Hz.

	δ(H)	δ(C)	HMBC (H → C)
H_a–C(1)	1.79–1.85 (*m*)	38.4	C(3), C(5)
H_b–C(1)	1.53–1.62 (*m*)		C(3)
H_a–C(2)	1.71–1.76 (*m*)	28.1	C(1), C(3)
H_b–C(2)	1.71–1.76 (*m*)		C(3)
H_α–C(3)	3.24 (*dd*, *J* = 10.9, 4.9)	79.0	C(2), C(4), C(5), C(23), C(24)
C(4)		38.6	
H_α–C(5)	0.72–0.76 (*m*)	55.0	C(3), C(4), C(23), C(24)
H_a–C(6)	1.53–1.62 (*m*)	18.3	
H_b–C(6)	1.53–1.62 (*m*)		
H_a–C(7)	1.47–1.52 (*m*)	32.7	
H_b–C(7)	1.29–1.34 (*m*)		
C(8)		39.8	
H_α–C(9)	1.53–1.62 (*m*)	47.1	C(1),C(8), C(10), C(11), C(14), C(25), C(26)
C(10)		36.8	
H_a–C(11)	1.92–1.97 (*m*)	23.6	C(9), C(10)
H_b–C(11)	1.80–1.84 (*m*)		C(8), C(9), C(12), C(13)
H–C(12)	5.31 (*t*, *J* = 3.4)	129.0	C(9), C(11), C(14), C(18)
C(13)		138.0	
C(14)		41.1	
H_a–C(15)	2.11–2.19 (*m*)	29.6	
H_b–C(15)	1.68–1.74 (*m*)		
H_a–C(16)	1.86–1.90 (*m*)	25.9	
H_b–C(16)	1.86–1.90 (*m*)		
C(17)		50.9	
H_β–C(18)	2.86 (br. *s*)	53.1	C(12), C(13), C(14), C(16), C(17), C(19), C(20), C(22), C(28), C(29)
C(19)		73.1	
H_β–C(20)	1.07–1.13 (*m*)	41.0	
H_a–C(21)	1.73–1.79 (*m*)	34.2	
H_b–C(21)	1.73–1.79 (*m*)	–	
H_α–C(22)	5.03 (*t*, *J* = 3.2)	76.2	C(16), C(17), C(18), C(20), C(1′)
Me(23)	0.99 (*s*)	27.9	C(3), C(5), C(24)
Me(24)	0.76 (*s*)	15.4	C(3), C(5), C(23)
Me(25)	0.96 (*s*)	16.0	
Me(26)	0.77 (*s*)	18.0	
Me(27)	1.22 (*s*)	24.3	
C(28)		178.0	
Me(29)	1.25 (*s*)	27.2	C(18), C(19)
Me(30)	0.94 (*d*, *J* = 6.0)	16.5	C(19), C(20), C(21)
C(1′)		165.4	
H–C(2′)	5.55 (*s*)	116.0	C(1′), C(4′), C(5′)
C(3′)		157.2	
Me(4′)	1.82 (*s*)	27.2	C(1′), C(2′), C(3′)
Me(5)	2.12 (*s*)	20.2	C(1′), C(2′), C(3′)

range interactions of both of them with H_b–C(1) in the ^{1}H,^{1}H-COSY spectrum, as suggested earlier by various authors [20] for this system, as well as HMBC connectivities (*Table 3*) of H_a–C(25) with C(1), C(3), C(5) and C(10), and of H_b–C(25) with C(1), C(5), and C(10), supported our assignment.

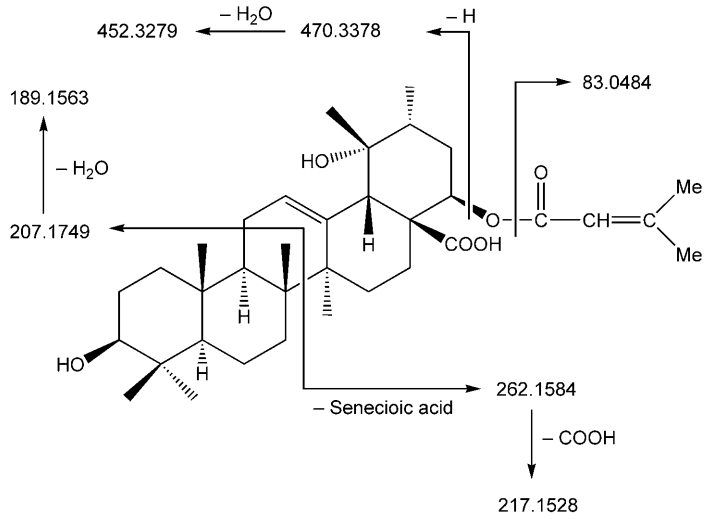


Fig. 2. *Key mass fragmentation of* **2** (in *m*/*z*)

The spectroscopic data of **3** again suggested a β-oriented (senecioyl)oxy function at C(22) [δ(H) 5.12 (*t*, J=3.0 Hz, 1 H); δ(C) 74.5 (CH)], in accord with MS fragments at *m/z* 83.0490 ($C_5H_7O^+$) and 482.3028 ($C_{30}H_{42}O_5^+$) (*Fig. 3*) and ^{1}H-NMR resonances at δ(H) 1.85 (*s*, Me(4′)) and 2.10 (*s*, Me(5′)), as well as a signal at δ(H) 5.60 (*s*, H–C(2′)). This was confirmed by the corresponding ^{13}C-NMR values assigned to this moiety through HMQC and HMBC experiments (*Table 3*). The connectivities of H_α–C(22) with C(16), C(17), C(18), C(20), and C(1′) in the HMBC spectrum confirmed the 22-position of the ester moiety.

The COOH group in **3** was indicated in the IR spectrum and confirmed by methylation with diazomethane [δ(H) 3.52 (*s*, COOMe)]. This function was located at C(17) by comparing the ^{13}C-NMR values of rings *D* and *E* with those of similar compounds [10][17]. Compound **3** further had an α,β-unsaturated C=O moiety (IR: 1690 cm^{-1}; UV: λ_{max} 248 nm), which was placed at C(11) due to the presence of a *singlet* at δ(H) 5.74 (H–C(12)) and ^{13}C-NMR signals [19] at δ(C) 198.5 (C(11)), 127.8 (C(12)), and 168.7 (C(13)). HMBC Connectivities of H–C(9) (δ(H) 2.45) with C(8), C(10), C(11), C(12), C(14), C(25), and C(26), and of H–C(12) (δ(H) 5.74) with C(8), C(9), C(11), C(13), C(14), C(18), and C(27), supported this assignment. The remaining O-atom was placed at C(3) as an α-oriented OH group as part of the hemiacetal, as there was no further CH signal in the ^{1}H-NMR spectrum. From the above data, the structure of camarinin (**3**) was identified as (22β)-3β,25-epoxy-3-hydroxy-22-[(3-methylbut-2-enoyl)oxy]-11-oxoolean-12-en-28-oic acid.

The seven known compounds isolated, oleanolic acid [6], ursolic acid [7], pomolic acid [8], lantanolic acid [9], camangeloyl acid [10], lantaninilic acid [11], and lantoic acid [12], were identified through comparison of their spectroscopic and mass-spectrometric data with published values.

Table 3. *^{1}H- and ^{13}C-NMR Data of Camarinin* (**3**). At 400/100 MHz, resp., in $CDCl_3$; δ in ppm, J in Hz.

	δ(H)	δ(C)	HMBC (H → C)
H_a–C(1)	2.07–2.13 (*m*)	34.7	C(2), C(3), C(5), C(25)
H_b–C(1)	1.16–1.24 (*m*)		
H_a–C(2)	1.48–1.54 (*m*)	27.9	C(3), C(4), C(10)
H_b–C(2)	1.27–1.33 (*m*)		
C(3)		99.0	
C(4)		38.5	
H_α–C(5)	1.09–1.15 (*m*)	51.1	C(3), C(4), C(23), C(24), C(25)
H_a–C(6)	1.46–1.56 (*m*)	19.1	
H_b–C(6)	1.46–1.56 (*m*)		
H_a–C(7)	1.46–1.56 (*m*)	30.9	
H_b–C(7)	1.29–1.33 (*m*)		
C(8)		43.9	
H_α–C(9)	2.45 (*s*)	55.6	C(8), C(10), C(11), C(12), C(14), C(25), C(26)
C(10)		35.3	
C(11)		198.5	
H–C(12)	5.74 (*s*)	127.8	C(8), C(9), C(11), C(13), C(14), C(18), C(27)
C(13)		168.7	
C(14)		43.7	
H_a–C(15)	2.07–2.16 (*m*)	29.6	
H_b–C(15)	1.73–1.79 (*m*)		
H_a–C(16)	1.84–1.90 (*m*)	23.6	
H_b–C(16)	1.84–1.90 (*m*)		
C(17)		50.3	
H_β–C(18)	3.16 (*dd*, J = 14.1, 4.2)	39.5	C(12), C(13), C(14), C(17), C(19), C(28)
H_a–C(19)	1.68–1.74 (*m*)	44.4	
H_b–C(19)	1.23–1.29 (*m*)		
C(20)		30.2	
H_a–C(21)	1.73–1.81 (*m*)	37.6	
H_b–C(21)	1.46–1.56 (*m*)		
H_α–C(22)	5.12 (*t*, J = 3.0)	74.5	C(16), C(17), C(18), C(20), C(1′)
Me(23)	1.11 (*s*)	27.4	C(3), C(5), C(24)
Me(24)	0.76 (*s*)	18.5	C(3), C(5), C(23)
H_a–C(25)	4.50 (*dd*, J = 8.4, 2.7)	65.7	C(1), C(3), C(5), C(10)
H_b–C(25)	4.02 (*dd*, J = 8.4, 1.1)		C(1), C(5), C(10)
Me(26)	0.92 (*s*)	18.8	
Me(27)	1.37 (*s*)	23.1	
C(28)		177.7	
Me(29)	0.90 (*s*)	33.6	
Me (30)	1.00 (*s*)	26.0	
C(1′)		165.1	
H–C(2′)	5.60 (*s*)	115.7	C(1′), C(4′), C(5′)
H–C(3′)		157.7	
Me(4′)	1.85 (*s*)	27.4	C(1′), C(2′), C(3′)
Me(5′)	2.10 (*s*)	20.3	C(1′), C(2′), C(3′)

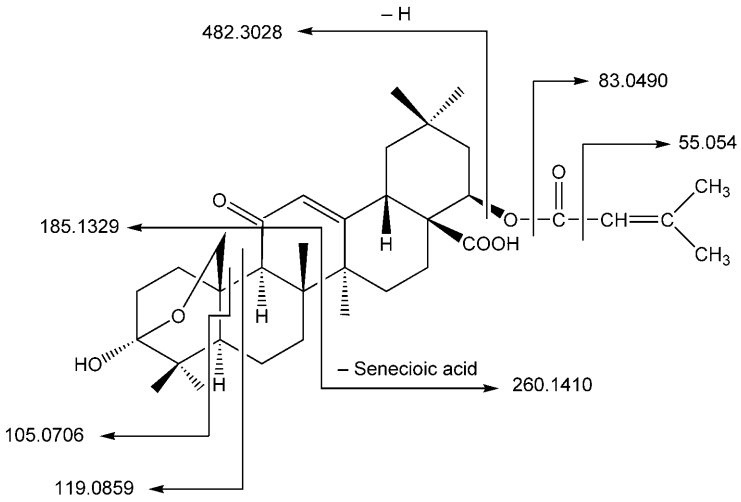


Fig. 3. *Key mass fragmentation of* **3** (in *m*/*z*)

Experimental Part

General. Vacuum liquid chromatography (VLC): silica gel *60 PF$_{254}$* (*Merck*). Flash chromatography (FC): *Eyela Flash Column EF-10* chromatograph; silica gel *9385* (0.040–0.063 mm; *Merck*). Prep. and anal. TLC: silica gel *60 PF$_{254}$* (*Merck*) and *Kieselgel Si F$_{254}$* (*Merck*) precoated Al plates (0.2 mm thickness), resp.; detection by exposure to I_2. UV Spectra: *Hitachi U-3200* spectrophotometer; λ_{max} in nm. IR Spectra: *Jasco A-302* spectrophotometer; in cm^{-1}. 1D- and 2D-NMR Spectra: *Bruker Avance* apparatus; at 300, 400, or 500 MHz (^1H), or at 75, 100, or 125 MHz (^{13}C), resp.; chemical shifts δ in ppm. rel. to Me_4Si, coupling constants *J* in Hz. EI-MS (70 eV): *Finnigan MAT-311A* mass spectrometer; source at 250°; in *m/z* (rel. %). HR-EI-MS (70 eV): *Jeol JMS-HX-110* mass spectrometer; source at 250°.

Plant Material. The aerial parts of *Lantana camara* LINN. 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) was deposited at the Herbarium.

Extraction and Isolation. *a*) The air-dried aerial parts of *L. camara* (10 kg) were repeatedly extracted with MeOH at r.t. The combined extracts, which exhibited nematicidal and antibacterial activities, were concentrated under reduced pressure, and the residue was partitioned between AcOEt and H_2O. The org. 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 over active charcoal, which was washed successively with AcOEt and MeOH/C_6H_6 1:1. The eluate fractions were combined on the basis of TLC analysis. The residue obtained on removal of the solvent was divided into petroleum ether (PE)-soluble and PE-insoluble fractions. The PE-insoluble one was subjected to VLC (PE/AcOEt gradient of increasing polarity): 14 fractions (*LC-1* to *LC-14*). Fraction *LC-2* (1.4 g; PE/AcOEt 9:1 and 8:2) was subjected to FC (PE, PE/AcOEt gradient of increasing polarity): 24 fractions (*Fr. 1* to *Fr. 24*). *Fr. 8* (eluted with PE/AcOEt 9:1) afforded **1** (12.0 mg). Fraction *LC-3* (3.0 g; eluted with PE/AcOEt 8:2) was resubjected to VLC (PE, PE/AcOEt gradient of increasing polarity): eleven subfractions (*LC-3.1* to *LC-3.11*). *LC-3.4* (521 mg) (eluted with PE/AcOEt 8:2) was subjected to FC ($CHCl_3$/MeOH gradient of increasing polarity) to afford oleanolic acid (9.0 mg; $CHCl_3$), ursolic acid (8.0 mg, $CHCl_3$), pomolic acid (8.0 mg, $CHCl_3$), **2** (10 mg; $CHCl_3$), and lantanolic acid (8.0 mg; $CHCl_3$/MeOH 99:1) in order of polarity.

b) In another purification, the above main PE-insoluble fraction was divided into Et_2O-soluble and -insoluble fractions. The latter was again divided into Et_2O-soluble and -insoluble portions. The AcOEt-soluble one was subjected to VLC ($CHCl_3$, $CHCl_3$/MeOH gradient in order of increasing polarity): nine

fractions (*Fr. A* to *Fr. I*). *Fr. A* (26.0 g; eluted with $CHCl_3$, $CHCl_3$/MeOH 99:1) was further subjected to VLC (PE, PE/AcOEt gradient of increasing polarity): eight fractions (*Fr. A.1* to *Fr. A.8*). *Fr. A.4* (9.3 g; eluted with PE/AcOEt 8:2, 7:3) was further subjected to VLC (PE, PE/AcOEt gradient of increasing polarity): 12 subfractions (*Fr. A.4.1–A.4.12*). *Fr. A.4.10* (PE/AcOEt 2:8, 1:9) gave four major spots on TLC, which, on repeated separation by prep. TLC ($CHCl_3$/MeOH 95:5), afforded **3** (10 mg), camangeloyl acid (7.0 mg), lantaninilic acid (4.0 mg), and lantoic acid (3.5 mg) in order of polarity.

Camarin (=*(7α)-7-Hydroxy-3-oxoolean-12-en-28-oic Acid*; **1**). Colorless crystalline solid. M.p. 255–256°. UV (MeOH): 206. IR ($CHCI_3$): 3420–2610, 2920, 2850, 1700, 1620, 1120. ^{1}H- and ^{13}C-NMR: see *Table 1*. EI-MS: 470 (38, M^+), 452 (4), 408 (4), 248 (100). 221 (5), 203 (93), 133 (34). HR-EI-MS: 470.0339 (M^+, $C_{30}H_{46}O_4^+$; calc. 470.3395), 452.3350 ($[M-H_2O]^+$, $C_{30}H_{44}O_3^+$), 408.3437 ($[M-H_2O-CO_2]^+$, $C_{29}H_{44}O^+$), 248.1794 ($C_{16}H_{24}O_2^+$), 221.1539 ($C_{14}H_{21}O_2^+$), 203.1435 ($C_{14}H_{19}O^+$), 203.1786 ($C_{15}H_{23}^+$), 133.1011 ($C_{10}H_{13}^+$).

Methylation of **1**. Compound **1** (2.5 mg) was esterified by treatment with an ethereal soln. of CH_2N_2, followed by the usual workup. ^{1}H-NMR ($CDCl_3$): 3.64 (*s*, COOMe). EI-MS: 484 (M^+).

Lantacin (=*(3β,19α,22β)-3,19-Dihydroxy-22-[(3-methylbut-2-enoyl)oxy]urs-12-en-28-oic Acid*; **2**). Colorless, amorphous powder. UV (MeOH): 217. IR ($CHCI_3$): 3428–2650, 2920, 2855, 1730, 1710, 1620, 1150. ^{1}H- and ^{13}C-NMR: see *Table 2*. EI-MS: 570 (6, M^+), 470 (18), 452 (6), 408 (14), 262 (30) 217 (41), 207 (97), 189 (17). HR-EI-MS: 570.3918 (M^+, $C_{35}H_{54}O_6^+$; calc. 570.3920), 470.3378 ($C_{30}H_{46}O_4^+$, [*M* – senecioic acid]$^+$), 452.3279 ($[M-$ senecioic acid $-H_2O]^+$, $C_{30}H_{44}O_3^+$), 408.3395 ($[M-$ senecioic acid $-H_2O-CO_2]^+$, $C_{29}H_{44}O^+$), 262.1584 ($C_{16}H_{22}O_3^+$), 217.1528 ($C_{15}H_{21}O^+$), 207.1749 ($C_{14}H_{23}O^+$), 189.1563 ($C_{14}H_{21}^+$).

Methylation of **2**. Compound **2** (2.5 mg) was methylated by treatment with an ethereal soln. of CH_2N_2, followed by the usual workup. ^{1}H-NMR ($CDCl_3$): 3.60 (*s*, COOMe). EI-MS: 584 (M^+).

Camarinin (=*(22β)-3β,25-Epoxy-3-hydroxy-22-[(3-methylbut-2-enoyl)oxy]-11-oxoolean-12-en-28-oic acid*; **3**). Colorless, amorphous powder. UV (MeOH): 248, 218. IR ($CHCI_3$): 3450–2650 (br.), 2941, 2852, 1730, 1700, 1690, 1620. ^{1}H- and ^{13}C-NMR: see *Table 3*. EI-MS: 582 (6, M^+), 564 (18), 519 (91), 482 (6), 466 (14), 419 (93), 419 (97), 260 (5), 242 (3), 185 (17), 133 (31), 119 (50), 105 (41), 55 (100). HR-EI-MS: 582.3546 (M^+, $C_{35}H_{50}O_7^+$; calc. 582.3556), 564.3448 ($C_{35}H_{48}O_6^+$), 519.3470 ($C_{34}H_{47}O_4^+$), 482.3028 ([*M* – senecioic acid]$^+$, $C_{30}H_{42}O_5^+$), 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 ($C_{30}H_{42}O_5^+$), 185.1329 ($C_{14}H_{17}^+$), 133.1018 ($C_{10}H_{13}^+$), 119.0859 ($C_9H_{11}^+$), 105.0706 ($C_8H_9^+$).

Methylation of **3**. Compound **3** (2.8 mg) was esterified by treatment with an ethereal soln. of CH_2N_2, followed by the usual workup. ^{1}H-NMR ($CDCl_3$): 3.52 (*s*, COOMe). EI-MS: 596 (M^+).

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