

## THE STRUCTURE AND STEREOCHEMISTRY OF A TRITERPENE ACID FROM *LANTANA CAMARA*

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**Key Word Index**—*Lantana camara*; Verbenaceae; triterpene; lantoic acid.

**Abstract**—The structure of lantoic acid, a new triterpene isolated from the leaves of *Lantana camara*, has been determined as 3,25-epoxy-3 $\alpha$ ,22 $\beta$ -dihydroxy-ursa-12-ene-28-oic acid by chemical and spectroscopic means.

### INTRODUCTION

The isolation of three new triterpene acids, lantanolic acid [1, 2], lantic acid [3, 4] and lantanilic acid [5, 6], has been reported from this laboratory. Several new triterpenes from *Lantana Camara* L. have been reported by John *et al.* [7] and Noel and co-workers [8]. The present paper reports the structure of another new triterpene acid, called lantoic acid (**1a**), from the petrol extract of the same plant.

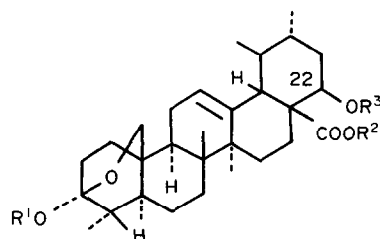
### RESULTS AND DISCUSSION

Lantoic acid (**1a**) was isolated in pure form as its methyl ester (**1b**),  $C_{31}H_{48}O_5$ , mp 208°,  $[\alpha]_D^{23} + 127.8^\circ$  ( $CHCl_3$ ) from a lantoic acid sample obtained by column chromatography and TLC on silica gel of the unsaponifiable lipid fraction of the crude triterpene acid mixture from a petrol extract of *L. camara*. It gave a pale yellow colour with tetranitroaniline and its UV spectrum showed maxima at 207 nm (log  $\epsilon$  3.8) indicating the presence of a tri-substituted double bond. The mass spectrum of methyl lantoate (**1b**) showed the  $[M]^+$  peak at  $m/z$  500 and a strong peak at  $m/z$  482  $[M - H_2O]^+$ . The mass spectral fragmentation pattern of methyl lantoate [ $m/z$  482, 260 (**a**), 299 (**b**) and 239 (**c**)] was very similar to that of methyl lantanilate [6] ( $m/z$  482, 260, 299 and 239). Methyl lantoate formed a ketal (**1c**),  $C_{32}H_{50}O_5$  ( $[M]^+$   $m/z$  514), mp 201–202° (dec.), on reflux with methanolic sulphuric acid, which on treatment with dilute hydrochloric acid in tetrahydrofuran gave back methyl lantoate (cf. methyl lantanilate) [6] and methyl lantate [3].

The ketal (**1c**) on acetylation with pyridine and acetic anhydride yielded an amorphous monoacetate (**1d**),  $C_{34}H_{52}O_6$ . The ketal (**1c**) on treatment with  $POCl_3$  in pyridine gave the dehydro compound **2** which was not isolated in a pure state but was hydrogenated over Adam's catalyst. The product thus obtained was identified as the ketal (**3**) of methyl lantate. This proved the structure of lantoic acid except for the position of the secondary hydroxyl group.

Formation of the ion species **a**, **b** and **c** in the mass spectrum of methyl lantoate clearly showed the presence of the secondary hydroxyl group either in ring D or in ring E of methyl lantoate. The  $^1H$ NMR spectrum ( $CDCl_3$ , 90 MHz) of methyl lantoate was very similar to that of

methyl lantate, except for the signal for H-22 $\alpha$  which was merged with the signal centred at  $\delta$  3.89 for one of the protons of the hemiketal system. It showed two pairs of doublets centred at  $\delta$  4.26 (1H,  $J = 9$  Hz) and 3.89 (1H,  $J$

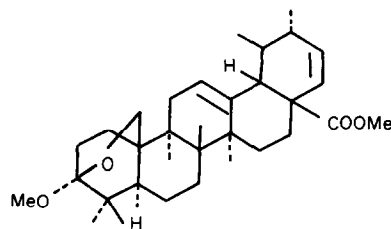


**1a**  $R^1 = R^2 = R^3 = H$

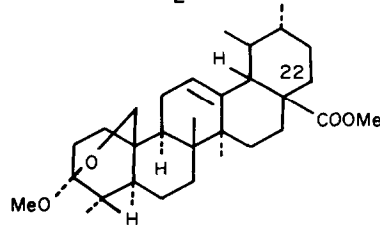
**1b**  $R^1 = R^3 = H, R^2 = Me$

**1c**  $R^1 = R^2 = Me, R^3 = H$

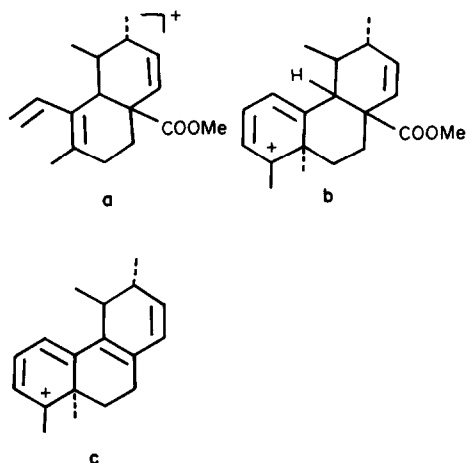
**1d**  $R^1 = R^2 = Me, R^3 = Ac$



**2**



**3**



= 9 Hz) for the two non-equivalent methylene protons ( $-\text{CH}_2-\text{O}-\text{C}-\text{O}-$ ) of the hemiketal system. These two signals were further split ( $J = 2.5$  Hz and 1 Hz respectively) due to long-range coupling with one of the C-1 protons. A sharp singlet at  $\delta 3.65$  (3H,  $-\text{COOMe}$ ) and a multiplet at  $\delta 5.35$  (1H) were due to the carbomethoxyl group and the C-12 vinyl proton, respectively. The  $^1\text{H}$  NMR spectrum in the high-field region showed five sharp singlets at  $\delta 0.70$  (3H),  $0.90$  (3H),  $0.97$  (6H),  $1.03$  (3H) and  $1.07$  (3H) corresponding to the six tertiary methyl groups. This portion of the spectrum was very similar to that of methyl lantate [3]. The appearance of the highest methyl signal at  $\delta 0.70$  indicated the presence of a carbomethoxyl group at C-17, since the highest methyl signal in triterpenes of the oleanane and ursane series having a carbomethoxyl group at C-17 appears upfield from  $\delta 0.775$  [9].

The  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 90 MHz) of the acetate (**1d**) showed a signal at  $\delta 4.97$  (1H,  $J = 3$  Hz) for H-22 $\alpha$  (cf.  $\delta 4.95$  for the H-22 $\alpha$  in the  $^1\text{H}$  NMR spectrum of the monoacetate of methyl lantanilic acid [6]). The low coupling constant ( $J = 3$  Hz) indicated an axial  $\beta$ -orientation of the secondary hydroxyl group at C-22. It

may be pointed out that in all triterpenes having a secondary hydroxyl group in ring E isolated from *L. camara*, the secondary hydroxyl group is invariably located at C-22. In some cases, the 22-OH was esterified with  $\beta,\beta$ -dimethyl acrylic acid, tiglic acid or angelic acid.

Most probably lantolic acid (**1a**) does not occur as such in the plant but occurs as its 22 $\beta$ -acryloyl, 22 $\beta$ -angeloyl or 22 $\beta$ -tigloyl derivative. This conclusion has been drawn because TLC of the crude triterpene acid fraction obtained from the petrol extract of the leaves of *L. camara* did not show any spot corresponding to that of lantolic acid.

Thus the spectral data and other data presented above indicate the structure of lantolic acid to be **1a**.

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