

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 α ,22 β -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.

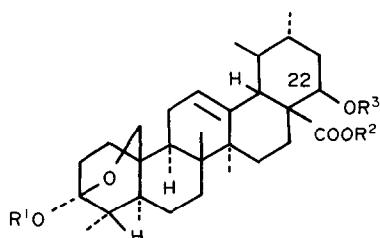
RESULTS AND DISCUSSION

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 lantanilinate [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 lantanilinate) [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 δ 3.89 for one of the protons of the hemiketal system. It showed two pairs of doublets centred at δ 4.26 (1H, $J = 9$ Hz) and 3.89 (1H, J

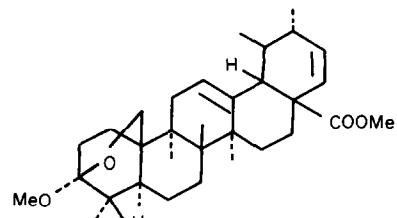


1a $R^1 = R^2 = R^3 = H$

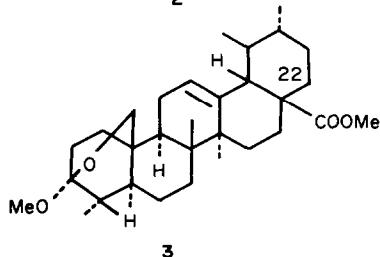
1b $R^1 = R^3 = H$, $R^2 = Me$

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

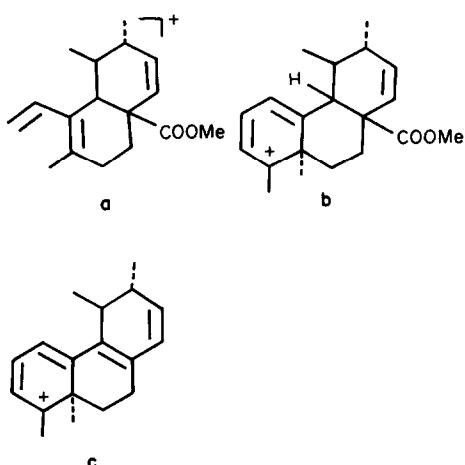
1d $R^1 = R^2 = Me$, $R^3 = Ac$



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 δ 3.65 (3H, $-\text{COOMe}$) and a multiplet at δ 5.35 (1H) were due to the carbomethoxyl group and the C-12 vinyl proton, respectively. The ^1H NMR spectrum in the high-field region showed five sharp singlets at δ 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 δ 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 δ 0.775 [9].

The ^1H NMR spectrum (CDCl_3 , 90 MHz) of the acetate (**1d**) showed a signal at δ 4.97 (1H, $J = 3$ Hz) for $\text{H}-22\alpha$ (cf. δ 4.95 for the $\text{H}-22\alpha$ in the ^1H NMR spectrum of the monoacetate of methyl lantanilate [6]). The low coupling constant ($J = 3$ Hz) indicated an axial β -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 β,β -dimethyl acrylic acid, tiglic acid or angelic acid.

Most probably lantoic acid (**1a**) does not occur as such in the plant but occurs as its 22 β -acryloyl, 22 β -angeloyl or 22 β -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 lantoic acid.

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

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