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THE FULL STRUCTURES OF LANSIC ACID AND ITS MINOR CONGENER, AN UNSYMMETRIC ONOCERADIENEDIONE

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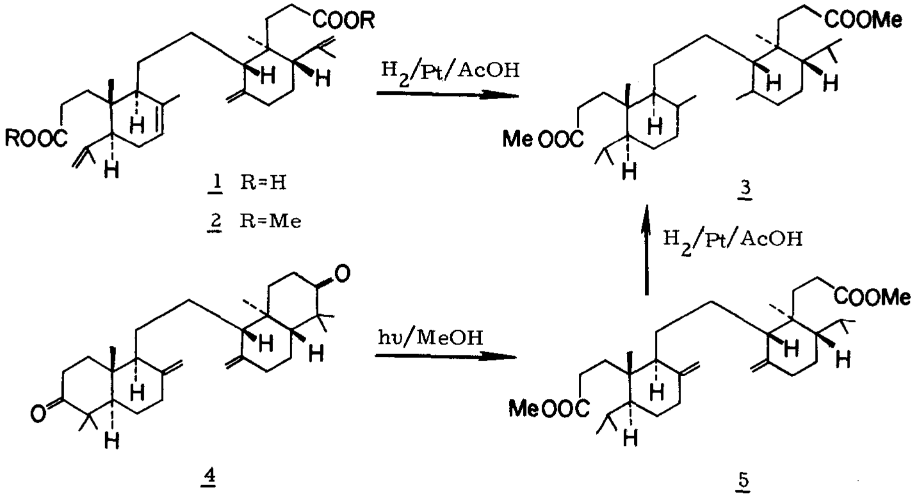
The planar structure of the bicyclic triterpene, lansic acid from Lansium domesticum fruit peel, has been reported in a previous communication.[1)] The following experiments correlate lansic acid with α-onocerin, and therefore the stereochemistry of lansic acid is established as indicated by 1.



1 R=H

2 R=Me

3

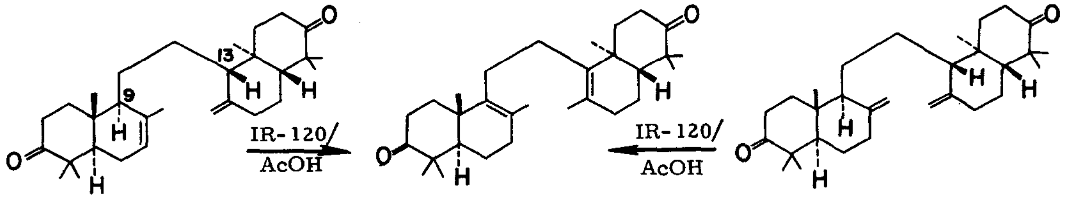
4

5

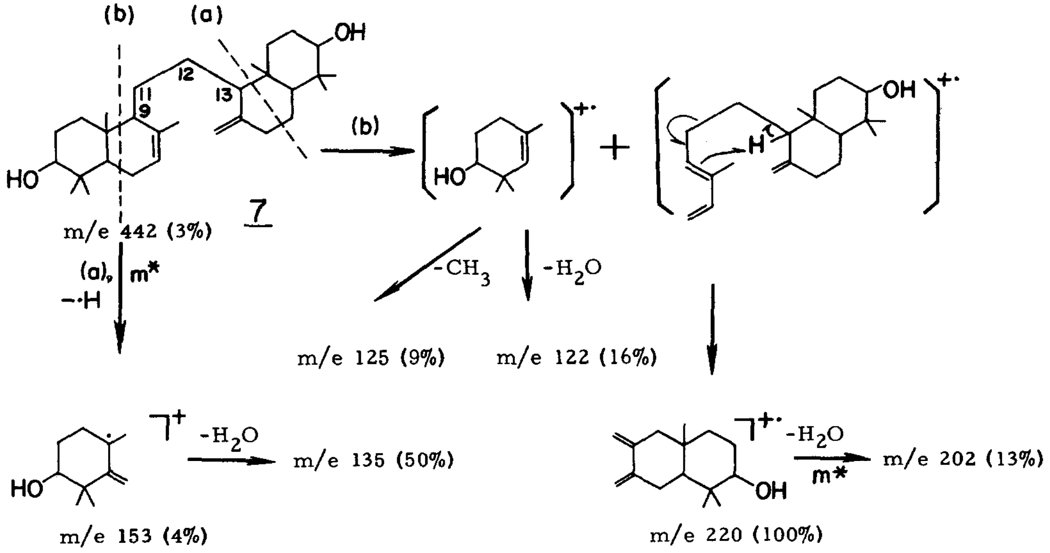
Hydrogenation of methyl lansate 2 afforded the octahydro derivative 3 as the major product which was separated by preparative TLC, oil, NMR (CDCl$_3$) 0.78 (6H, d, J 4 cps, sec-Me), 0.83 (12H, d, J 4 cps, isopropyl Me), 0.98 (6H, s, tert-Me), and 3.64 ppm (6H, s, COOMe); I R (nujol) 1745 cm^{-1} (COOMe). α-Onoceradienedione, m.p. 183-185°,[2)] in methanol was irradiated[3, 4)] for 6 hours with a 450 W high-pressure mercury lamp to give the oily dimethyl ester 5, NMR ($CDCl_3$) 0.63 (6H, s, tert-Me), 0.75 and 0.90 (both 6H, d, J 7 cps, isopropyl-Me), 3.66 (6H, s, COOMe), 4.87 and 4.57 ppm (both 2H, broad s, exocyclic methylene), as the major product, which was separated by preparative TLC. Hydrogenation of 5 afforded the fully saturated ester 3, identical [IR, NMR, ORD (plain positive, 260-600 mμ in dioxane), TLC] with the compound derived from lansic acid, and this establishes the entire stereochemistry of this bicyclic triterpene composed of two unsymmetric halves.

The petroleum ether extract of the skin powder afforded besides lansic acid, a minor constituent after working up with silica gel column chromatography and TLC. On the basis of the following data, structure 6 is assigned to this congener, $C_{30}H_{46}O_2$ (M^+ at 438), m. p. 127-128°, ORD (c 1.05 mg/ml in dioxane) $[\phi]^{tr}_{316}$ -2980, $[\phi]^{pk}_{270}$ +1340, a -43.2; NMR ($CDCl_3$) Me singlets at 0.87, 0.97, 1.02, 1.05, 1.13 and 1.13 ppm, olefinic Me (C_8) at 1.68 ppm coupled to olefinic H (C_7) at 5.44 ppm, exocyclic methylene protons at 4.63 and 4.95 ppm; IR (KBr) 1710 and 887 cm^{-1}. Lithium aluminum hydride reduction of 6 gave the diol 7, $C_{30}H_{50}O_2$ (M^+ at 442), m. p. 108-110°, the NMR spectrum of which showed an additional broad two-proton signal at 3.10-3.40 ppm due to carbinyl protons. The mass spectrum of the diol 7 is composed of peaks resulting from cleavages due to the endocyclic and exocyclic double bonds[1] as shown in the figure.

When the minor constituent was heated at 70° for 20 hours in acetic acid with the cation exchange resin Amberlite IR-120, i. e., conditions which affected cyclizations of methyl trans, trans-farnesate,[5] it was quantitatively converted into the dienedione 8, m. p. 169-170°, ORD (c 0.85 mg/ml in dioxane) $[\phi]^{pk}_{301}$ +4330, $[\phi]^{tr}_{274}$ +2930, a +14.0. The same (m. p., rotation, IR, NMR, TLC) compound, namely, β-onoceradienedione,[2] was obtained upon identical IR-120 treatment[5] of α-onoceradienedione 9, m. p. 183-185°,[2] ORD (c 1.1 mg/ml in dioxane) $[\phi]^{tr}_{320}$ -1340, $[\phi]^{pk}_{288}$ +880, a -22.2. This establishes the configurations at the various asymmetric centers excepting C-9 and C-13, but in view of the structure of the major lansic acid 1, the configurations as indicated in structure 6 are assigned. The minor constituent is probably a precursor in the biosynthesis of lansic acid.



6 8 9



Note: Cleavage between bonds 9-11 and/or 12-13 gives peaks at m/e 207 (7%) $\xrightarrow{-H_2O}$ m/e 189 (11%).

The unsymmetric arrangements of double bonds in these two triterpenes should be noted, besides the fact that lansic acid is the first bicyclic triterpene in which rings A and E have both undergone cleavage of the type encountered in ring A of dammarenolic acid,[4] nyctanthic acid,[4, 6] roburic acid[7] and canaric acid.[8]

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