

X-Ray Crystal and Molecular Structure of the Bromolactone of Echinocystic Acid Diacetate. The Absolute Configuration of Naturally Occurring Oleananes

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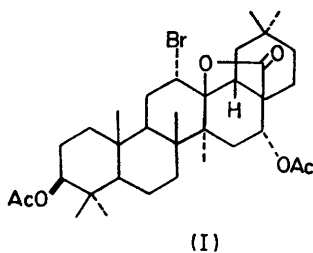
Summary X-ray analysis of the title compound settles recent controversy concerning the configuration at C-16 of several 16-hydroxy-oleananes.

HYDROXYLATION at C-16 is a common feature of the β -amyrin group of triterpenoids.¹ Recently it has been suggested that the configuration at C-16 of several of these compounds should be reversed.² The only evidence presented was that the presence of a *trans*-diaxial 16 α ,28-diol system was not consistent with the observed formation of a diacetone from olean-12-ene-3 β ,16 α ,23,28-tetraol (derived from natural quillaic acid). The required changes

contradict the large amount of chemical and n.m.r.³ data supporting the previously assigned configurations, and do not take account of a recent, stereochemically defined, synthesis of echinocystic acid.⁴

We consider that the results of Segal and Taube are better explained in terms of conformational mobility in rings D and E, a phenomenon previously proposed⁵ to rationalise acetyl migration from C-16 α to C-28 in primulagenin A. This contention has been strengthened by the recent report⁶ that both olean-12-ene-3 β ,16 α ,28-triol and olean-12-ene-3 β ,16 β ,28-triol form acetone derivatives. We now report an X-ray analysis of the bromo-lactone (I)⁷ derived

from natural echinocystic acid which establishes unequivocally that the previously accepted structures for echinocystic acid and related^{1,2,8} compounds are correct.



Crystal data; $C_{34}H_{51}O_6Br$, $M = 635.7$, monoclinic, $a = 9.051(1)$, $b = 10.229(1)$, $c = 18.019(2)$ Å, $\beta = 96.00(1)^\circ$, $U = 1659$ Å³, $D_m = 1.28$, $Z = 2$, $D_c = 1.27$, $F(000) = 676$, space group $P2_1$, μ (Cu- K_α) = 22.1 cm⁻¹.

Crystals of the bromo-lactone (I) are colourless, monoclinic, and sphenoidal. Preliminary cell dimensions and space group information were obtained from precession and Weissenberg photographs using copper radiation. Refined

cell dimensions and intensity data were measured on a Hilger-Watts Y290 automatic four-circle diffractometer. The intensities of approximately 3000 reflections were obtained in the range $0^\circ \leq 2\theta \leq 120^\circ$. The deterioration of the crystal in the X-ray beam was monitored by measuring three reference reflections after every 50 reflections and scaling the data to these references; an overall decrease of 10% was observed in the intensities of the reference reflections. The data were corrected for Lorentz and polarisation effects but no correction was made for absorption.

The structure was determined by the heavy-atom method. It is at present stereochemically correct but not accurate. Refinement is in progress, using a full matrix least-squares method, and with all non-hydrogen atoms treated isotropically; the current value of R is 0.14. In the unrefined structure the acetoxy group at C-16 is axial (α) and *trans* to the lactone ring.

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