

## Revised Structure for the Photoisomer of 11-Oxolanostanol; a Synthesis of Cycloartanol<sup>1</sup>

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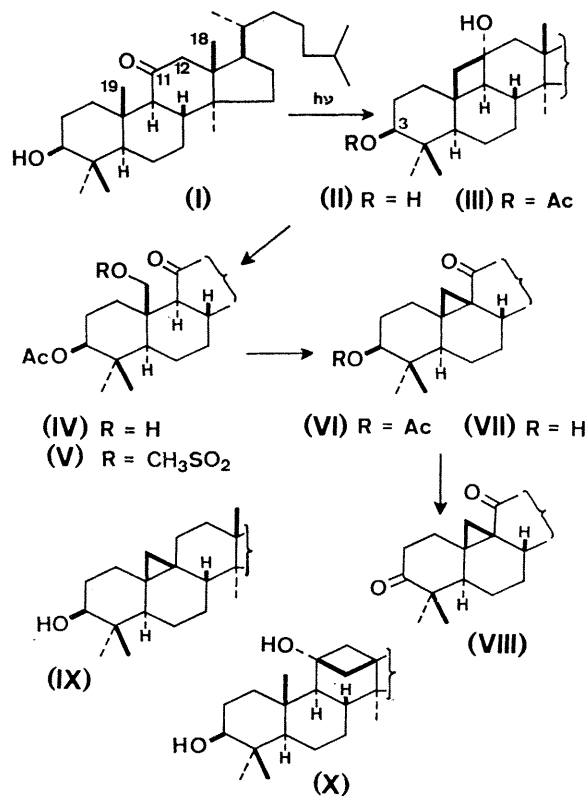
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**Summary** Re-formulation of the photoproduct of 11-oxolanostanol as (II) on the basis of recent disclosures in the literature establishes previously published work as a total (formal) synthesis of cycloartanol.

We have previously reported<sup>2</sup> on the u.v. irradiation of 11-oxolanostanol (I) as part of a synthetic approach to the dihydro-derivative (IX) of the triterpenoid cycloartanol. Our approach was based on the observation that 11-oxosteroids [including a 4,4-dimethyl-5 $\alpha$ -H derivative closely related to (I)] are photoisomerised in high yield to 11 $\alpha$ -hydroxy-11 $\beta$ ,19-cyclobutanes.<sup>3</sup> Irradiation of (I) in ethanol furnished<sup>2</sup> an isomeric tertiary cyclobutanol in over 50% yield based on reacted starting material. However, when this was subjected to the procedure<sup>3</sup> which should have converted it into the cyclopropyl diketone (VIII), the product clearly differed (direct comparison) from material previously obtained by a different route and formulated by Barton, Budhiraja and McGhie<sup>4</sup> as (VIII). We consequently assigned to our photolysis product the structure (X), although this appeared less attractive mechanistically<sup>5</sup> and was seemingly at variance with recorded precedent.<sup>3</sup>

We now have been led to reconsider our earlier conclusions by a recent publication<sup>6</sup> which describes the preparation of the compounds (VI) and (VIII), whose physical properties closely resemble those of the appropriate derivatives previously obtained from our photolysis product.† Furthermore, the substance, reputedly (VIII),<sup>4</sup> which had served us for comparison, has subsequently been re-formulated.<sup>7</sup> We have now directly compared our cyclopropyl ketone acetate, previously formulated as 11-oxo-12 $\beta$ ,18-cyclolanostanyl acetate,<sup>2</sup> with Corsano's 11-oxocycloartanyl

acetate (VI)<sup>‡</sup> and found them to be identical. The photolysis product of (I) therefore clearly has the structure



† Our sample of compound (VIII), previously assigned the 12 $\beta$ ,18-cyclolanostane-3,11-dione structure,<sup>2</sup> has m.p. 107–108°, [ $\alpha$ ]<sub>D</sub> + 95° (c 0.36, CHCl<sub>3</sub>); lit.<sup>6</sup> m.p. 111–113°, [ $\alpha$ ]<sub>D</sub> + 95°. The values reported earlier<sup>2</sup> are erroneous.

‡ Agreement with respect to m.p., specific rotation, i.r. and mass spectra, t.l.c. using several solvent systems, and no depression of the mixed m.p. We thank Professor S. Corsano for a sample of 11-oxocycloartanyl acetate (VI).

(II) originally expected and the compounds obtained from it must be re-formulated accordingly [*cf.* (III)—(VIII)§].

In the light of this re-evaluation our previously published work<sup>2</sup> constitutes a total (formal) synthesis of cycloartanol (IX), since lanosterol, from which (I) was prepared,<sup>8</sup> has

been synthesised *via* cholesterol,<sup>9</sup> and (VI) has been converted into (IX).<sup>6,10</sup>

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§ Corresponding re-formulations apply also, of course, for the 3-oxo- and 3-ethyleneacetal derivatives of (II) which were described in the previous report.<sup>2</sup>

<sup>1</sup> For previous paper in this series see D. Belluš and K. Schaffner, *Helv. Chim. Acta*, 1969, **52**, 1010.

<sup>2</sup> E. Altenburger, H. Wehrli, and K. Schaffner, *Helv. Chim. Acta*, 1965, **48**, 704.

<sup>3</sup> H. Wehrli, M. S. Heller, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, 1961, **44**, 2162; M. S. Heller, H. Wehrli, K. Schaffner, and O. Jeger, *ibid.*, 1962, **45**, 1261; J. Iriarte, K. Schaffner, and O. Jeger, *ibid.*, 1963, **46**, 1599.

<sup>4</sup> D. H. R. Barton, R. P. Budhiraja, and J. F. McGhie, *Proc. Chem. Soc.*, 1963, 170.

<sup>5</sup> For a recent discussion, see O. Jeger and K. Schaffner, *Pure Appl. Chem.*, 1969, in the press.

<sup>6</sup> S. Corsano and G. Nicita, *Ricerca Sci.*, 1967, **37**, 351.

<sup>7</sup> D. H. R. Barton, R. P. Budhiraja, and J. F. McGhie, *J. Chem. Soc. (C)*, 1969, 336.

<sup>8</sup> W. Voser, M. Montavon, Hs. H. Günthard, O. Jeger, and L. Ruzicka, *Helv. Chim. Acta*, 1950, **33**, 1893.

<sup>9</sup> R. B. Woodward, A. A. Patchett, D. H. R. Barton, D. A. J. Ives, and R. B. Kelly, *J. Chem. Soc.*, 1957, 1131, and references therein.

<sup>10</sup> For the synthesis of cycloartenol, see D. H. R. Barton, D. Kumari, P. Welzel, L. J. Danks, and J. F. McGhie, *J. Chem. Soc. (C)*, 1969, 332.