

32-HYDROXYLATED LANOSTANE DERIVATIVES BY PHOTOLYSIS

OF 3 $\beta$ -ACETOXY-7-KETOLANOSTANE<sup>1</sup>

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Recent communications from this,<sup>2,3</sup> and other<sup>4,5,6</sup> laboratories have described syntheses of biogenetically important 32-oxygenated lanostane derivatives, in which functionalization of the 32-methyl group was achieved by intramolecular attack of an oxygen radical generated from a 7 $\alpha$ -hydroxyl group. We now wish to report on an alternative synthesis of 3 $\beta$ ,32-dihydroxy- $\Delta^7$ -lanostene (VI), in which such functionalization has been effected via the photochemically excited 7-keto group.<sup>7</sup> Irradiation<sup>8</sup> of 3 $\beta$ -acetoxy-7-ketolanostane (I)<sup>9</sup> in ethanol for 75 minutes furnished on direct crystallization in 63% yield<sup>10</sup> the 7,32-cyclosteroid II,<sup>11</sup> m.p. 152-153°;  $[\alpha]_D^{37} +10^\circ$ ;  $\lambda_{\max}^{\text{KBr}}$  2.88 $\mu$  (7 $\beta$ -OH), 5.75 and 5.85 $\mu$  (3 $\beta$ -acetyl); n.m.r. 5.50 $\tau$  (m. 3 $\alpha$ H), 7.96 $\tau$  (3-acetyl), quartet centered at 7.15 $\tau$  (2 protons, 32-CH<sub>2</sub>), which was cleaved with lead tetraacetate in benzene in presence of CaCO<sub>3</sub> (16 hours) to furnish in 60% yield the hemiketal IIIa, m.p. 230-232° (after drying at 100°, 239-241°);  $[\alpha]_D^{35} +22^\circ$ ;  $\lambda_{\max}^{\text{KBr}}$  2.94 $\mu$  (7 $\beta$ -OH), 5.76 $\mu$  (3 $\beta$ -acetyl), no 7-keto band; n.m.r. 5.97 $\tau$  (d. J = 8 cps) and 6.48 $\tau$  (d. J = 8 cps, one proton each, 32-CH<sub>2</sub>). Recrystallization of IIIa from methanol containing a trace of acid afforded in quantitative yield the cyclic methyl ketal IIIb, m.p. 150-151°;  $[\alpha]_D^{35} +10^\circ$ ; n.m.r.



and its smooth dehydration with  $\text{SOCl}_2$  in pyridine at  $0^\circ$  for 40 min. to afford  $3\beta,32$ -diacetoxy- $\Delta^7$ -lanostene (VI),<sup>3</sup> m. p.  $122-122.5^\circ$ ,  $[\alpha]_D^{29} +27^\circ$ , identical in all respects with an authentic sample of this substance.<sup>13</sup> Hydrolysis of VI with KOH in methanol at  $25^\circ$  gave the  $3\beta,32$ -diol, m. p.  $204-205^\circ$ ,  $[\alpha]_D^{35} +10^\circ$ .

#### REFERENCES

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8. Irradiation was effected at  $25^\circ$  with a 200 W. Hanovia quartz high pressure mercury lamp without filter.
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10. In contrast, irradiation of  $3\beta$ -acetoxy-7,11-diketolanostane and  $3\beta$ -acetoxy-

$\Delta^{9(11)}$ -7-ketolanostane under similar conditions led to complex mixtures as shown by GLC from which no crystalline products could be isolated.

11. Correct analytical figures were obtained for all crystalline compounds. Analyses by J. Alicino, Metuchen, N. J. Melting points are corrected. Rotations in  $\text{CHCl}_3$ . N. m. r. spectra in  $\text{CDCl}_3$ .
12. Compound Va was recovered unchanged after 3 hours. Acetylation was complete after 75 hours at  $25^\circ$ . Cf. ref. 3 for acetylation of  $3\beta,7\alpha$ -lanostanediol.
13. These constants differ slightly from those reported in ref. 3 for a sample, which has since been found to be contaminated with a substance of identical  $R_F$  (TLC) and retention time (GLC) formed in the acetolysis of the  $7\alpha,32$ -oxide, probably  $3\beta,7\beta,32$ -triacetoxylanostane. We wish to express our appreciation to Professor Barton for supplying us with a sample of pure VI prepared by his procedure, which led to the discovery of the impurity in our sample.