# Studies of Artefacts of the Acid Treatment of (23*S*)-Lanosta-8,24-diene-3β,23-diol

By **Norman Entwistle** * and **Alexander D. Pratt**, School of Chemistry, University of Bradford, Bradford 7

Under acidic conditions in ethanol the side-chain of (23*S*)-lanosta-8,24-diene-3β.23-diol undergoes an allylic rearrangement to yield lanosta-8.23-diene-3β.25-diol. 25-ethoxylanosta-8.23-dien-3β-ol. and (23*S*)- and (23*R*)-23-ethoxylanosta-8.24-dien-3β-ol. Under stronger acid conditions. loss of the elements of water from the side chain occurs to give lanosta-8.22,24-trien-3β-ol.

(23*S*)-LANOSTA-8,24-DIENE-3β,23-DIOL,[1,2] obtained from the Basidiomycete *Scleroderma aurantium* Pers., was found to be acid-labile, undergoing an allylic rearrangement of the side-chain to yield lanosta-8,23-diene-3β,25-diol (2), along with 25-ethoxylanosta-8,23-dien-3β-ol (3), and (23*S*)- and (23*R*)-23-ethoxylanosta-8,24-dien-3β-ol [(4) and (5), respectively]. These products were separated by p.l.c.
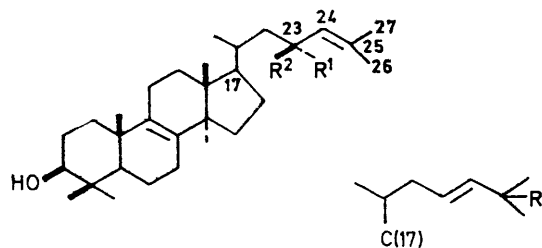


(1) R¹ = H, R² = OH
(4) R¹ = H, R² = OEt
(5) R¹ = OEt, R² = H

(2) R = OH
(3) R = OEt

The analysis and i.r. spectrum of diol (2) confirmed that it was isomeric with the starting material (1). Acetylation yielded only a monoacetate, indicating that the unmodified hydroxy-group is in a tertiary position. The mass spectrum of diol (2) is almost identical with that of diol (1) although the peak intensities are different. The dihydro-derivative of (2) only forms a monoacetate.

From this evidence, compound (2) was deduced to be lanosta-8,3-diene-3β,25-diol and this structure was confirmed by $^1$H n.m.r. studies and by degradation. The $^1$H n.m.r. spectrum of (2) and of its dihydro-derivative show the 3β-proton quartet at τ 6·84, typical of 3β-hydroxylanostanes. The absence of other C*H*OH signals confirms the presence of a tertiary hydroxy-group. Furthermore the presence of this hindered hydroxy-group at C-25 is indicated by a six-proton singlet at τ 8·74 due to the equivalent C-26 and C-27 methyl protons and typical of a substituted propan-2-ol.[3] On saturation of the side-chain double bond of (2) these signals appear at slightly higher field, τ 8·85, indicating the magnitude of the deshielding of the C-26 and C-27 methyl protons in diol (2) by this alkene linkage. For this deshielding to be at all appreciable one would expect the bond to be located in the nearest available position to the equivalent methyl protons because the magnitude of deshielding is greatly dependent on the distance between the two entities.[4a] On this basis the double bond should be situated in the 23,24-position.

The dihydro-derivative of (2) was identical with lanost-8-ene-3β,25-diol synthesised from lanosterol *via* the 24,25-epoxy-derivative.

Degradation of the side-chain of (2) was carried out by ozonolysis to yield an oil which contained an aldehyde ($\nu_{max.}$ 1723 cm$^{-1}$); the oil was treated with sodium borohydride to give the more easily handled alcohol. P.l.c. of the reduced product yielded a diol with a molecular

[1] N. Entwistle and A. D. Pratt, *Tetrahedron*, 1968, **24**, 3949.
[2] N. Entwistle and A. D. Pratt, *Tetrahedron*, 1969, **25**, 1449.
[3] C. Djerassi and R. McCrindle, *J. Chem. Soc.*, 1962, 4034.
[4] L. M. Jackmann, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, London, 1963, (*a*) p. 113, (*b*) p. 85.

ion peak at $m/e$ 386 ($M^+$, 386·3190. $C_{26}H_{42}O_2$ requires $M$, 386·3185) instead of the expected $m/e$ 388. The u.v. and i.r. spectra showed that during ozonolysis the 8,9-double bond had been converted into the familiar 7,9(11)-diene system,[5] and this product was assigned as 24,25,26,27-tetranorlanosta-7,9(11)-diene-3β,23-diol.
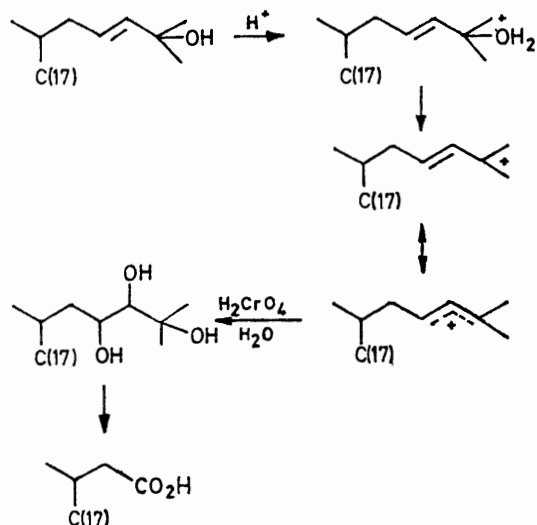


SCHEME 1

The corresponding acid, 3β-hydroxy-24,25,26,27-tetranorlanost-8-en-23-oic acid ($M^+$, 402·3130. $C_{26}H_{42}O_3$ requires $M$, 402·3133) was also obtained.

Jones oxidation of diol (2) gave 3-oxo-24,25,26,27-tetranorlanost-8-en-23-oic acid. Tertiary alcohols are relatively inert to oxidation; we suggest a mechanism involving a mesomeric cation to account for this reaction (Scheme 1). The 100 MHz n.m.r. spectrum of lanosta-8,23-diene-3β,25-diol would be expected to exhibit a two-proton pattern in the olefinic region, of basically four lines with typical $J$ values for protons situated on a *trans*-disubstituted double bond (*i.e.* 11—18 Hz).[4b] The signals should then show fine structure due to the possible vicinal and allylic interactions within the system. The C-23 and C-24 protons give a two-proton complex pattern at τ 4·49, and the two protons appear to be nearly isochronous.[6] This must be a consequence of the small inductive deshielding effect of the C-25 hydroxy-group and the deshielding due to the anisotropy of the magnetic susceptibility of the C–O bond which, by their influence principally on the C-24 proton, cause the magnetic fields experienced by both olefinic protons to be nearly the same.

Compounds (3)—(5) from the reaction of the parent diol (1) were obtained in higher yield by treating (1) in ethanol with twice the amount of N-sulphuric acid used in the preparation of compound (2). Compound (3) formed a monoacetate, and contained two carbon atoms

more than diol (1); these carbon atoms are present as an ethoxy-group (ether C–O–C stretching band in the i.r. spectrum). The mass spectrum exhibits a peak at $m/e$ 424 [$M^{+\cdot}$ — 46 ($CH_3 \cdot CH_2 \cdot OH$); $m^*$ 382·4] which indicates the loss of ethanol by fission of the ethoxy C–O bond and rearrangement of one hydrogen atom.[7] The mass spectral fragmentation pattern below $m/e$ 409 is identical with that of compound (2). On this evidence, compound (3) is considered to be 25-ethoxylanosta-8,23-dien-3β-ol.

Only small quantities of compounds (4) and (5) were obtained and their structures could be deduced only from spectroscopic evidence. Their i.r. spectra are identical; each shows a strong ether C–O–C stretching absorption at 1080, a hydroxy C–O absorption at 1030, and moderately strong absorptions at 1675 and 840 cm⁻¹ indicative of a trisubstituted double bond. Their mass spectra are identical, with molecular ion peaks at $m/e$ 470 ($M^+$, 470·4146. $C_{32}H_{54}O_2$ requires $M$, 470·4124). The peak at $m/e$ 273 indicates that the triterpenoid nucleus is the same as that in the parent diol (1), and the ethoxy-group is shown by the peak at $m/e$ 424 [$M^{+\cdot}$ — 46 (EtOH)]. The fragmentation leading to the formation of the base peak at $m/e$ 113 helps in the location of the ethoxy-group; this peak is not present in the mass spectrum of the hydroxy-ether (3), and its origin is explained if both compounds (4) and (5) contain a 24,25-double bond and an ethoxy-group at C-23. Cleavage will take place to give the resonance-stabilized ion (a).
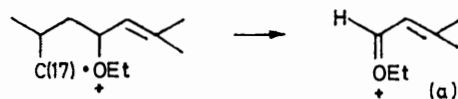


Although compounds (4) and (5) do not differ spectrally, they exhibit different polarities during t.l.c. This difference is explained by their being epimeric at C-23. By analogy with the polarities of the C-23 epimers of lanosta-8,24-diene-3β,23-diol,[2] it seems reasonable that the more polar of the two ethers is the ethoxy-ether of the more polar of the two diols. On this basis, compounds (4) and (5) are (23S)- and (23R)-23-ethoxy-lanosta-8,24-dien-3β-ol, respectively.

The formation of compounds (2)—(5) would be expected from the anionotropic rearrangement of the side-chain. The formation of the epimeric C-23 ethers (4) and (5) by racemization when the reaction ' reverses ' is adequate confirmation of the mechanism. Treatment of any of the three ethyl ethers (3)—(5) in ethanol with 0·05M-sulphuric acid resulted in the establishment of the equilibrium mixture. In the anionotropic relationship between the parent diol (1) and the diol (2), the former might be expected to be the more stable because of the greater stabilization of the 24,25-double bond, owing to the hyperconjugative effect of the 25-methyl groups.

[5] D. Rosenthal, P. Grabowich, E. F. Sabo, and J. Fried, *J. Amer. Chem. Soc.*, 1963, **85**, 3971.

[6] M. van Gorkom and G. E. Hall, *Quart. Rev.*, 1968, **22**, 15.

[7] H. Budzikiewicz, C. Djerassi, and D. H. Williams, ' Interpretation of the Mass Spectra of Organic Compounds,' Holden–Day, San Francisco, 1964, p. 51.

T.l.c. results show that the equilibrium lies far to the right; thus the oxotropic mobility is high. The driving
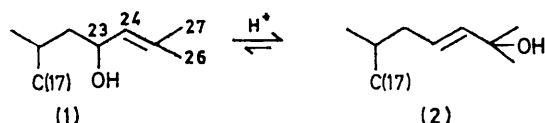


force of the reaction is the greater stability of the intermediate tertiary carbocation than of the secondary carbocation. Similar reactions have been reported (conversion of hexa-2,5-dienol into hexa-2,4-dienol[8] and of 3-methylhexa-2,5-dienol into 1-methylhexa-2,4-dienol[9]). Treatment of either diol (1) or (2) with greater concentrations of mineral acid (chloroform saturated with concentrated hydrochloric acid) results in the loss of water and the formation of a major component (6) ($C_{30}H_{48}O$). U.v. and i.r. spectra indicate the presence of a conjugated diene, and hydrogenation yields lanost-8-en-3β-ol. Loss of water has taken place from the side-chain. In the mass spectrum, the base peak ion (b), $m/e$ 109, arises by allylic fission of the C(17)–C(20) bond; the appearance of this peak is evidence for the presence of the 22,24-diene system (Scheme 2). Ozono-



$C_8H_{13}$ $m/e$ 109 (b)
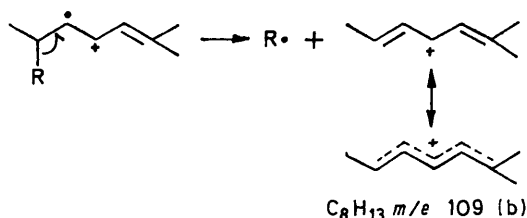
SCHEME 2

lysis of the trienol (6) followed by reduction with sodium borohydride yielded apparently one major product which was isolated by p.l.c. Molecular ion peaks at $m/e$ 402 and 374 indicated the presence of two diols (7) and (8), formed as shown in Scheme 3. An explanation for the
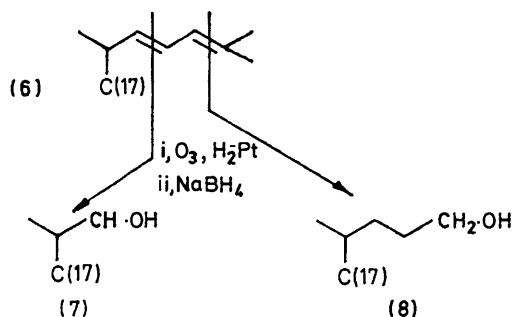


SCHEME 3

formation of the unexpected $C_{27}$ diol could be that formation of the C(24)–C(25) ozonide hinders attack by

[8] I. Heilbron, E. R. H. Jones, J. T. McCombie, and B. C. L. Weedon, *J. Chem. Soc.*, 1945, 84, 88.
[9] E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 1950, 2000, 2007.

ozone on the 22,23-double bond, and this double bond is then reduced during work-up.

Tertiary alcohols usually lose water under mild conditions. It is significant that the conditions used to dehydrate diol (2) are not effective for the dehydration of the dihydro-derivative of (2) (lanost-8-ene-3β,25-diol). The 23,24-double bond is therefore important in the reaction, which we suggest involves a mesomeric carbocation in an $E1$ scheme.

Theoretically, the dehydration of diol (2) to yield triene (6) could also yield the isomeric 23,25-diene by elimination of one of the six hydrogen atoms of the 25-methyl groups. After p.l.c. of the crude dehydration product, the faint, diffuse bands occurring at lower $R_F$ values than the major component (6) were recovered. Two of the bands yielded a colourless solid which did not crystallise but whose u.v. absorption at $\lambda_{max.}$ 230 nm corresponded well with the value calculated[10] for the 23,25-diene system. The solid was obviously a mixture but all attempts at purification were unsuccessful.

The 5-hydroxy-1,5-dimethylhex-3-enyl triterpene side-chain of the diol (2) is not novel, and has previously been found in cycloart-23-ene-3β,25-diol, isolated from *Tillandsia usneoides* (Spanish moss).[3] This metabolite occurs in the moss together with an isomeric diol, cycloart-25-ene-3β,24ξ-diol. Djerassi *et al.* assumed that these two compounds arose biogenically by the oxidative attack at one or other end of the olefinic linkage of the precursor cycloartenol followed by a shift of the double bond.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage. I.r. spectra (KBr discs) were recorded on a Perkin-Elmer model 237 spectrometer. N.m.r. spectra were determined on a Varian 100 Hz instrument. Optical rotations were determined for chloroform solutions at room temperature on a photoelectric polarimeter. U.v. spectra were determined for ethanolic solutions on a Unicam SP 800 spectrometer. Mass spectra were determined on an A.E.I. MS 902 spectrometer. T.l.c. was carried out on unactivated silica gel on glass with a stationary phase thickness of 0·2 mm and a developing solvent system of benzene–ethyl acetate (9 : 1). The spray reagent was an ethanolic solution of acetic anhydride and concentrated sulphuric acid whose application was followed by heating the plates at 110° for 10 min. P.l.c. was carried out on unactivated silica gel (Merck Kieselgel $PF_{254+366}$) on glass (100 × 20 cm) with a stationary phase thickness of 2 mm and a developing solvent system of benzene–ethyl acetate (9 : 1), and bands were extracted with ethyl acetate. All organic solutions were dried over anhydrous sodium sulphate.

*Isolation of Lanosta-8,23-diene-3β,25-diol* (2).—(23S)-Lanosta-8,24-diene-3β,23-diol (200 mg) in absolute ethanol (20 ml) was treated with N-sulphuric acid (1 ml). After 24 h the solution was diluted with water and extracted (3×) with ethyl acetate. The combined organic layers were washed with water, dried, and evaporated under

[10] A. I. Scott, 'The Ultraviolet Spectra of Natural Products,' Pergamon, London, 1964, p. 46.

reduced pressure, and the residue was purified by p.l.c. (2 elutions) to give *lanosta*-8,23-*diene*-3β,25-*diol* as square plates (from ethyl acetate) (119 mg), m.p. 160—164°, $M^{+\bullet}$ 442, $[\alpha]_D$ +43° ($c$ 0·30) (Found: C, 81·4; H, 11·2. $C_{30}H_{50}O_2$ requires C, 81·5; H, 11·3%), $\nu_{max.}$ (CHCl$_3$) 3610, 1024, and 973 cm$^{-1}$.

*Acetylation of Lanosta*-8,23-*diene*-3β,25-*diol*.—Acetylation of the diol using acetic anhydride–pyridine afforded 25-*hydroxylanosta*-8,23-*dien*-3β-*yl acetate* which was purified by p.l.c. and crystallized from ethyl acetate as rods, m.p. 122—124°, $[\alpha]_D$ +40° ($c$ 0·15) (Found: C, 78·6; H, 10·8. $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·7%; this compound consistently yielded poor analysis figures for carbon), $\nu_{max.}$ (CHCl$_3$) 3610, 1725, 1032, and 981 cm$^{-1}$.

*Hydrogenation of Lanosta*-8,23-*diene*-3β,25-*diol*.—The diol (100 mg) in ethanol (95%; 30 ml) was hydrogenated over Adams catalyst (30 mg) at 20° and atmospheric pressure until uptake ceased. The solution was filtered and evaporated under reduced pressure to yield lanost-8-ene-3β,25-diol which crystallized from ethyl acetate as small needles (77 mg), subliming at 172—180°, $M^{+\bullet}$ 444, $[\alpha]_D$ +60° ($c$ 0·32) (Found: C, 81·0; H, 11·6. Calc. for $C_{30}H_{52}O_2$: C, 81·1; H, 11·7%). The product was identical with an authentic sample prepared from lanosterol as described below.

*Acetylation of Lanost*-8-*ene*-3β,25-*diol*.—Acetylation of the diol using acetic anhydride–pyridine yielded 25-*hydroxylanost*-8-*en*-3β-*yl acetate* which crystallized from methanol as long rods, m.p. 167—168° (sublimes), $[\alpha]_D$ +56° ($c$ 0·30) (Found: C, 78·6; H, 11·1. $C_{32}H_{54}O_3$ requires C, 79·0; H, 11·1%), $\nu_{max.}$ (CHCl$_3$) 3600, 1723, and 1030 cm$^{-1}$.

*Oxidation of Lanosta*-8,23-*diene*-3β,25-*diol*.—Jones oxidation of the diol (200 mg) gave 3-*oxo*-24,25,26,27-*tetranorlanost*-8-*en*-23-*oic acid* as minute rods (90 mg) (from ethyl acetate), subliming above 210°, $M^{+\bullet}$ 400, $[\alpha]_D$ +62° ($c$ 0·23) (Found: C, 77·4; H, 10·1. $C_{26}H_{40}O_3$ requires C, 77·5; H, 10·0%), $\nu_{max.}$ (KBr) 3200br, 1726, and 1696 cm$^{-1}$.

The tetranor-acid, on treatment with an excess of ethereal diazomethane, yielded *methyl 3-oxo*-24,25,26,27-*tetranorlanost*-8-*en*-23-*oate*, which crystallized from methanol as needles, m.p. 124—126°, $M^{+\bullet}$ 414, $[\alpha]_D$ +58° ($c$ 0·16) (Found: C, 78·3; H, 10·0. $C_{27}H_{42}O_3$ requires C, 78·2; H, 10·1%), $\nu_{max.}$ (KBr) 1740 and 1707 cm$^{-1}$.

*Ozonolysis of Lanosta*-8,23-*diene*-3β,25-diol.—The diol (200 mg) was treated in ethyl acetate (15 ml) with a stream of ozonized oxygen for 12 min at −30°. The ozonide was decomposed by hydrogenation over Adams catalyst (20 mg) at 0—5° for 1 h. The resulting solution was filtered and evaporated under reduced pressure to yield a clear, viscous oil, which was treated in dioxan (10 ml) with sodium borohydride (800 mg) in aqueous dioxan (50%, 10 ml) over 1 h. Dilution with water, and decomposition of excess of reagent with dilute mineral acid was followed by ether extraction (3×). The extract was dried and evaporated, and the residue was purified by p.l.c. to give 24,25,26,27-*tetranorlanosta*-7,9(11)-*diene*-3β,23-*diol*, in low yield, which crystallized from methanol as stout rods (15 mg), m.p. 220—225° (sublimes), $M^{+\bullet}$ 386·3190 ($C_{26}H_{42}O_2$ requires $M$, 386·3185). Elution of a more polar diffuse band followed by further t.l.c. purification yielded a small amount of the above diol and 3β-*hydroxy*-24,25,26,27-*tetranorlanost*-8-*en*-

23-*oic acid*, which crystallized from methanol as irregular rods (8 mg), m.p. 143—148°, $M^{+\bullet}$ 402·3130 ($C_{26}H_{42}O_3$ requires $M$, 402·3133).

*Preparation of 24,25,26,27-Tetranorlanost*-8-*ene*-3β,23-*diol*.—Methyl 3-oxo-24,25,26,27-tetranorlanost-8-en-23-oate (30 mg) in dry ether (2 ml) was added to a slurry of lithium aluminium hydride (15 mg) in dry ether (5 ml) and the mixture was refluxed for 2 h. Excess of reducing agent was destroyed by careful addition of water and the product was extracted with ether (3×). The residue from evaporation of the dried extract was purified by p.l.c. and yielded 24,25,26,27-*tetranorlanost*-8-*ene*-3β,23-*diol*, which crystallized from methanol as irregular rods (11 mg), m.p. 194—197°, $M^{+\bullet}$ 388·3347 ($C_{26}H_{44}O_2$ requires $M$, 388·3341).

*Isolation of Compounds* (3)—(5).—(23S)-Lanosta-8,24-diene-3β,23-diol (200 mg) in ethanol (20 ml) was treated with N-sulphuric acid (2 ml). After 24 h the solution was diluted with water and extracted with ethyl acetate (3×). The combined organic layers were dried and concentrated and then subjected to p.l.c. (3 elutions) which gave the separate components (2) (37 mg), (3) (110 mg), (4) (19 mg), and (5) (25 mg).

25-*Ethoxylanosta*-8,23-*dien*-3β-*ol* (3) crystallized from methanol as needles, m.p. 145—146°, $M^{+\bullet}$ 470 (Found: C, 81·9; H, 11·3. $C_{32}H_{54}O_2$ requires C, 81·7; H, 11·5%), $\nu_{max.}$ (KBr) 3465, 1062, 1038, and 980 cm$^{-1}$. Treatment with acetic anhydride–pyridine gave 25-*ethoxylanosta*-8,23-*dien*-3β-*yl acetate* which crystallized from methanol as needles, m.p. 96—99° (Found: C, 79·2; H, 10·8. $C_{34}H_{56}O_3$ requires C, 79·7; H, 10·9%), $\nu_{max.}$ (KBr) 1740, 1247, 1072, 1036, and 978 cm$^{-1}$.

(23S)-23-*Ethoxylanosta*-8,24-*dien*-3β-*ol* (4) crystallized from methanol as irregular rods, m.p. 115—115·5°, $M^{+\bullet}$ 470·4146 ($C_{32}H_{54}O_2$ requires $M$, 470·4124) (Found: C, 81·5; H, 11·3. $C_{32}H_{54}O_2$ requires C, 81·7; H, 11·5%).

(23R)-23-*Ethoxylanosta*-8,24-*dien*-3β-*ol* (5) crystallized from methanol as long rods, m.p. 125—127°, $M^{+\bullet}$ 470·4146 (Found: C, 81·3; H, 11·3. $C_{32}H_{54}O_2$ requires C, 81·7; H, 11·5%).

*Preparation of 24,25-Epoxylanost*-8-*en*-3β-*yl Acetate*.—Purified lanosterol [11] was acetylated and then treated with *m*-chloroperbenzoic acid [12] by a published method,[13] to give the 24,25-epoxide.

*Reduction of 24,25-Epoxylanost*-8-*en*-3β-*yl Acetate*.—The epoxy-acetate (200 mg) was treated with lithium aluminium hydride as described above (6 h reflux). Usual work-up followed by p.l.c. gave *lanost*-8-*ene*-3β,25-*diol* as needles from ethyl acetate (40 mg), m.p. 172—180 (sublimes), $M^{+\bullet}$ 444 (Found: C, 80·9; H, 11·6. $C_{30}H_{52}O_2$ requires C, 81·1; H, 11·7%).

*Dehydration of Lanosta*-8,23-*diene*-3β,25-*diol*.—(23S)-Lanosta-8,24-diene-3β-23-diol (500 mg) was dissolved in chloroform (50 ml) which had been saturated with concentrated hydrochloric acid (equal volumes of chloroform and concentrated acid were shaken together for 3 h and the layers were allowed to separate overnight). After 24 h the solution was washed with water (5×), dried, and evaporated under reduced pressure. The waxy residue crystallized from methanol–chloroform and the crystalline solid (~400 mg) was then further purified in two batches by p.l.c. to give *lanosta*-8,22,24-*trien*-3β-*ol*, which crystallized from methanol as needles (253 mg), m.p. 131—133°,

[11] J. D. Johnston, F. Gautschi, and K. Bloch, *J. Biol. Chem.*, 1957, **224**, 185.
[12] L. S. Silbert, E. Siegel, and D. Swern, *Org. Synth.*, 1963, **43**, 93.

[13] M. Akhtar, P. F. Hunt, and M. A. Parvez, *Biochem. J.*, 1967, **103**, 620.

$M^{+\cdot}$ 424, $[\alpha]_D$ +55° ($c$ 0·33) (Found: C, 84·8; H, 11·1. $C_{30}H_{48}O$ requires C, 84·9; H, 11·3%), $\nu_{max.}$ (CHCl$_3$) 3612, 1650, 1618, 1020, and 989 cm$^{-1}$, $\lambda_{max.}$ 238·2 nm ($\varepsilon$ 18,960).

*Hydrogenation of Lanosta*-8,22,24-*trien*-3β-*ol*.—The trienol (50 mg) in ethyl acetate (30 ml) was hydrogenated at 20° and atmospheric pressure over Adams catalyst (20 mg) until uptake was complete. The solution was filtered and evaporated under reduced pressure, and the residue crystallized from methanol to yield lanost-8-en-3β-ol as needles, m.p. 138·5—141°, $[\alpha]_D$ +58° ($c$ 0·32) (Found: C, 83·7; H, 12·0. Calc. for $C_{30}H_{52}O$: C, 84·1; H, 12·1%), identical with an authentic sample (t.l.c. and i.r. and n.m.r. spectra).

*Ozonolysis of Lanosta*-8,22,24-*trien*-3β-*ol*.—The trienol (250 mg) in ethyl acetate (10 ml) was treated with a stream of ozonized oxygen at −30° until ozonolysis was complete. The ozonides were decomposed by hydrogenation over Adams catalyst (30 mg) in ethyl acetate (20 ml) at 0° and atmospheric pressure for 1 h. Filtration and evaporation of the solution under reduced pressure yielded a flaky solid, $\nu_{max.}$ (CHCl$_3$) 3600, 1722, and 1650 cm$^{-1}$. This solid in dioxan (10 ml) was treated with sodium borohydride (600 mg) in aqueous dioxan (50%; 10 ml) over 1 h at room temperature. Usual work-up and p.l.c. gave a product which crystallized from methanol as prisms (38 mg), m.p. 149—152° (Found: C, 80·4; H, 11·3. Calc. for $C_{25}H_{42}O_2$: C, 80·2; H, 11·2%. $C_{27}H_{46}O_2$ requires C, 80·6; H, 11·4%), $\nu_{max.}$ (KBr) 3390 and 1030 cm$^{-1}$. The mass spectrum of the product exhibited two molecular ion peaks, at $m/e$ 402 and 374 which indicated a mixture of 25,26,27-trinorlanost-8-ene-3β,24-diol and 23,24,25,26,27-pentanorlanost-8-ene-3β,22-diol.