Tetrahedron Vol 24, pp 2859 to 2880 Pergamon Press 1968 Printed in Great Britain

THE STRUCTURE AND THE STEREOCHEMISTRY OF ABIESLACTONE[1]

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(*Received in Japan* 31 *August* 1967; *accepted for publication* 21 *September* 1967)

Abstract—Abieslactone, a triterpenoid isolated from several firs (*Abies* spp.) has been shown to be 3α-methoxylanosta-9(11), 24-dien-27, 23R-olide (I).

ABIESLACTONE (I) is a triterpenoid first isolated by Takahashi[2] from the bark and leaves of *Abies mariesii* Masters (Pinaceae), a tall evergreen tree indigenous to mountains in the northern part of Japan. In a previous paper[3] this compound was assigned the molecular formula, $C_{31}H_{48}O_3$, based on repeated analyses and shown to probably have the skeleton of trimethylsteroids by selenium dehydrogenation. The identical compound has also been isolated independently from the bark of *A. amabilis* (Dougl.) Forbes (0·01 %)[2,4] and *A. procera* Rehd. by Dr. H. L. Hergert, Rayonier, Inc., in the United States and presented to one of the authors (J.W.R.) for investigation. Initially the research group in each country was undertaking investigation of the structure unknown to the other. Since, however, direct comparison has shown that they were working on the same compound, we decided to carry out a joint investigation on the structure and stereochemistry.

The molecular formula of abieslactone has now been supported by the parent peak at *m/e* 468 in the mass spectrum. Of the three O atoms in abieslactone, one could be attributed to the OMe group which was shown by the Zeizel method and the three-hydrogen singlet at τ 6·73 in the NMR spectrum. Two more O atoms were combined in an α,β-unsaturated γ-lactone. Titrimetric estimation of abieslactone indicated the presence of a lactone group that exhibited a maxima at 207·5 mμ (log ε 4·30) in the UV spectrum. The IR spectrum had a band at 1745 cm^{-1} that shifted to 1770 cm^{-1} on hydrogenation to a dihydro derivative II of abieslactone in which the triplet at τ 8·10 for the vinylic Me protons in the NMR spectrum of abieslactone disappeared and the six Me groups in the region of τ 8·98–9·08 were increased to seven (τ 8·68–9·08) with concomitant loss of a vinylic proton at τ 3·00. In agreement with this assumption, treatment of abieslactone with LAH gave as a result of reductive cleavage of the lactone ring the diol, III, which was characterized as the di-*p*-nitrobenzoate. The one-hydrogen vinylic multiplet at τ 4·48 in the NMR spectrum of abieslactone did not disappear readily on attempted hydrogenation at room temperature and atmospheric pressure, and only after prolonged hydrogenation over

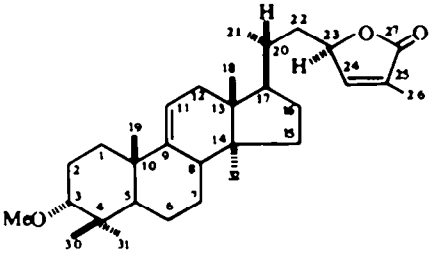
Adams catalyst in acetic acid–ethyl acetate were four H atoms taken up to give tetrahydroabieslactone (IV) which had no vinylic signals in the region of τ 3–4 in the NMR spectrum.

Permanganate oxidation of abieslactone in acetic acid by the procedure of Takahashi[2] gave a trisnorhydroxy-acid, V, with the loss of three C atoms from the starting material. The acid was characterized as the methyl ester (VI), the acetate (VII), and the methyl ester acetate (VIII). The IR spectra of the trisnorhydroxy acid (V) and its methyl ester (VI) exhibited CO bands at 1690 and 1725 cm^{-1}, respectively. These bands were at a lower frequency than the respective absorptions at 1710 and 1730 cm^{-1} of the corresponding acetyl derivatives (VII and VIII), due to intramolecular hydrogen bonding of the carboxyl group with the OH group suggesting that the OH group is geminal to the carboxyl in the trisnorhydroxy acid (V). The trisnorhydroxy acid methyl ester (VI) showed singlets at τ 8·93–9·30 corresponding to six C–Me protons, and a multiplet at τ 4·66 for one trisubstituted vinylic proton. These facts indicated that the lactone grouping in abieslactone was at the terminal position of the side chain and suffered a loss of three C atoms on permanganate oxidation as a result of cleavage of the double bond in the lactone ring followed by hydrolysis of the resulting ester grouping.

Alkaline hydrolysis of abieslactone gave, in analogy with angelicalactone,[4,5] the keto-acid IX, which exhibited a UV maximum at 276 mμ (log ε 1·72) and a ketone band at 1713 cm^{-1} in the IR. The keto-acid was characterized as the methyl ester (X) which showed CO bands at 1738 (COOMe) and 1715 cm^{-1} (CO) in the IR and gave a 2,4-dinitrophenylhydrazone. It reverted to abieslactone on heating with acetic anhydride. Attempted hydrogenolytic demethoxylation of this keto-ester was not successful; hydrogenation over Adams catalyst under 1700 lb/in^2 and 150° for 17 hr gave a mixture of products that on chromatographic separation afforded the saturated deoxo-ester (XI), a small amount of the corresponding deoxoacid (XII), and tetrahydroabieslactone (IV).

For the purpose of eliminating the oxygen functions on the side chain we first treated the keto-ester (X) with LAH to give the diol, XIII, which exhibited only one vinylic proton at τ 4·47 in contrast to the diol III obtained by LAH reduction of abieslactone itself. This yielded a monotosylate (XIV), which on treatment with LAH gave an oxide (XV) showing no OH band in the IR. Analogously, the diol XVI derived from tetrahydroabieslactone (IV) on treatment with LAH gave an oxide (XVII).

Since these attempts were not successful, we undertook an alternative sequence of reactions. The keto-ester (X) was treated with ethanedithiol in the presence of BF_3–etherate to give a thioketal (XVIII), which was desulfurized with Raney-nickel in boiling ethanol. The deoxo-ester (XIX) thus obtained, was reduced with LAH, giving rise to the alcohol, XX. This was tosylated and treated again with LAH to furnish the compound, XXIII, which exhibited NMR signals in the region of τ 8·93–9·35 corresponding to eight C-methyls and a one-hydrogen multiplet at τ 4·75 for a vinylic proton. The same compound was obtainable, though in a lower yield, on filtering the tosylate (XXI) through a column of alumina and subsequent hydrogenation of the resulting unsaturated compound (XXII). Hydrogenation of this compound (XXIII) under more drastic conditions gave a saturated compound, which was shown to be 3α-methoxylanostane (XXIV) as follows.



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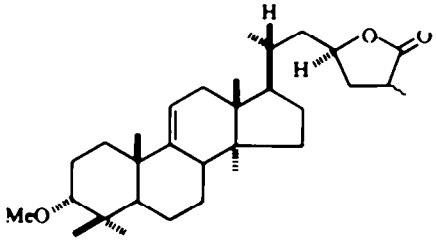

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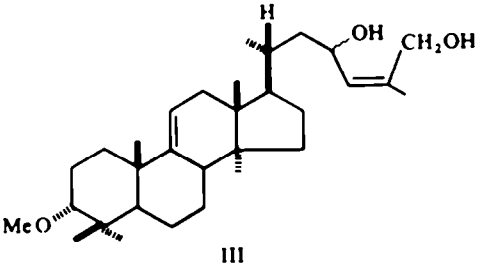

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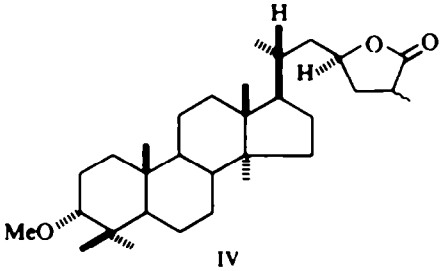

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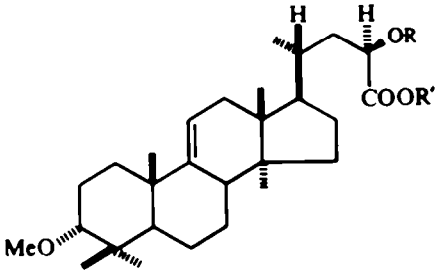
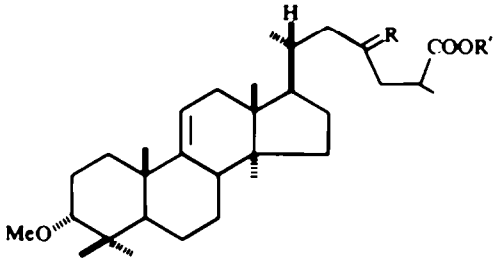
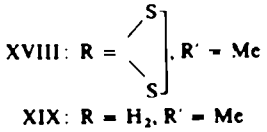


V: R = R′ = H
VI: R = H, R′ = Me
VII: R = Ac, R′ = H
VIII: R = Ac, R′ = Me

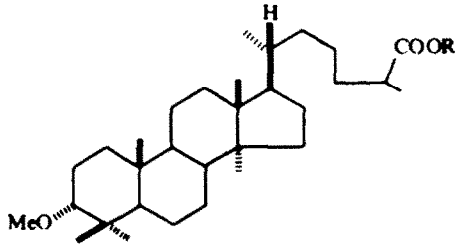


IX: R = O, R′ = H
X: R = O, R′ = Me

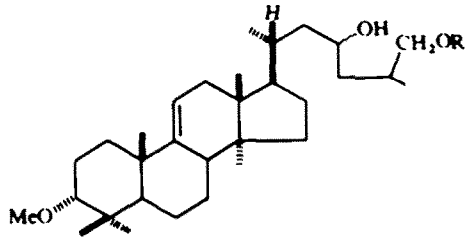


XVIII: R = , R′ = Me

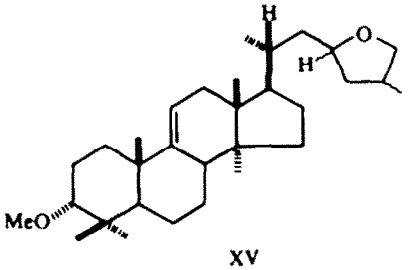
XIX: R = H_2, R′ = Me



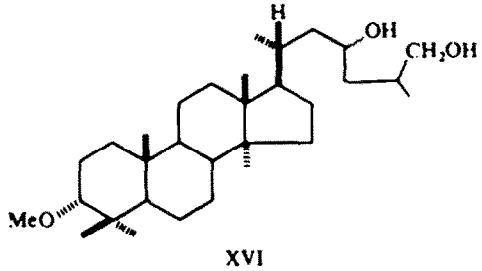
XI: R = Me
XII: R = H



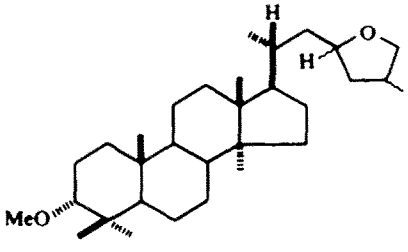
XIII: R = H
XIV: R = Ts



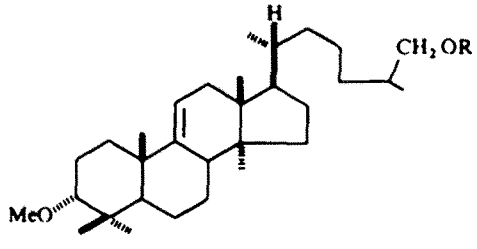
XV



XVI

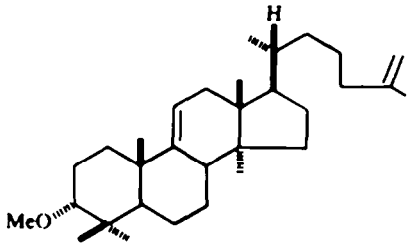


XVII

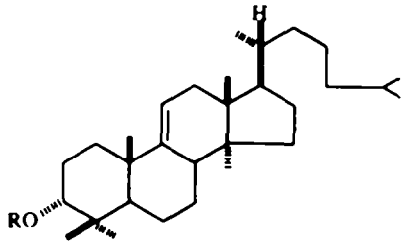


XX: R = H
XXI: R = Ts

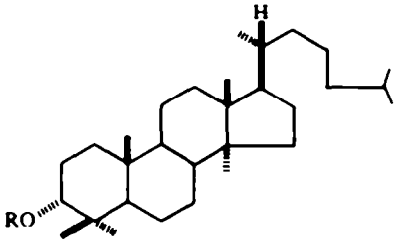
Demethylation of the OMe group in this compound (XXIV) was effected by the action of hydrobromic acid in acetic anhydride-acetic acid, affording the acetate, XXV, which was hydrolyzed with ethanolic potassium hydroxide to the alcohol, XXVI, m.p. 164–165°, $[\alpha]_D$ +21·5° ($CHCl_3$). This was not identical with lanostan-3β-ol (XXVIII),[6,7] but rather a C(3)-epimer, since it was smoothly converted by oxidation with chromic acid–pyridine complex into a ketone, m.p. 133–134°, $[\alpha]_D$ +28·4°, identical in all aspects with lanostan-3-one (XXVII).[6,7]



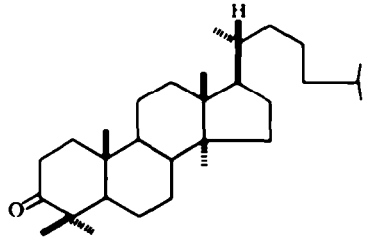
XXII



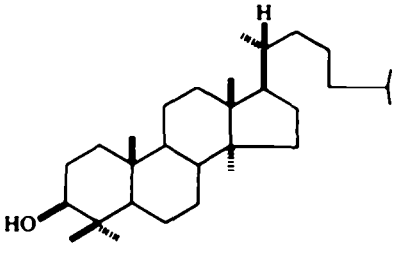
XXIII: R = Me
XXXV: R = Ac
XXXVI: R = H



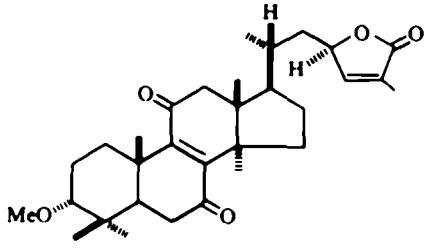
XXIV: R = Me
XXV: R = Ac
XXVI: R = H



XXVII



XXVIII



XXIX

The structure and the stereochemistry of the nucleus of abieslactone (I) have thus been elucidated. The OMe group has been established to be at C(3) and is presumably α-oriented and therefore axial. This is compatible with the interpretation of the NMR spectrum of the alcohol (XXVI) in which a one-hydrogen diffused triplet (J = 2·5 c/s) at τ 6·55 indicated that the H atom attached to C(3) is equatorial; hence the OH must be axial. Analogous one-hydrogen triplets were also observed for the acetoxyl and methoxyl derivatives, the acetoxyl derivative (XXV) showing a triplet

(J = 2·7 c/s) at τ 5·36 and the OMe derivative a triplet (J = 2 c/s) at τ 7·2. These findings indicated that no inversion of the oxygen function took place during the hydrolysis of the OMe group, and accordingly the OMe group at C(3) in abieslactone must be α-oriented and axial.

For comparison we have prepared 3β-methoxylanost-8-ene and 3β-methoxytirucall-8-ene[8] and confirmed that in the NMR, the axial hydrogen attached to C(3) bearing an equatorial OMe group exhibited a quartet different in shape from the corresponding signals of the abieslactone derivatives as shown in Table 1.

TABLE 1

Compound	H C^3(OMe) C^4—	OMe
Abieslactone	τ 7·20 triplet J = 1·8 c/s	τ 6·73
3α-Methoxylanost-9(11)-ene (XXIII)	τ 7·18 triplet J = 2·3 c/s	τ 6·70
3α-Methoxylanostane (XXIV)	τ 7·20 triplet J = 2·3 c/s	τ 6·70
3β-Methoxylanost-8-ene	τ 7·31 quartet J_{AX} = 10 c/s J_{BX} = 4 c/s	τ 6·63
3β-Methoxytirucall-8-ene	τ 7·31 quartet J_{AX} = 10 c/s J_{BX} = 4 c/s	τ 6·63

Now we turn to the location of the isolated double bond in abieslactone. Since it is trisubstituted as shown by the NMR spectrum and is in the steroidal ring-system as inferred from its resistance to hydrogenation under mild conditions, probable locations are limited to C(7)–C(8) and C(9)–C(11). This inference was supported by the following facts. Abieslactone on oxidation with chromic acid gave the compound, XXIX, containing a chromophore, CO—C=C—CO, as shown by its UV spectrum, λ_{max} 274 mμ (log ε 3·84). On oxidation with osmium tetroxide it afforded a tertiary secondary dihydroxy compound (XXX) as shown by its NMR spectrum that showed signals at τ 7·65 (1H, singlet) for a tertiary OH proton and at τ 5·95 (1H, multiplet) for a proton geminal to a OH group. This gave on periodide oxidation a keto-aldehyde (XXXI), although it was not obtained pure. Of the two possibilities, the position of the double bond between C(7)–C(8) could be ruled out because of the fact that abieslactone (I) and its derivative, XXIII, showed no facile shift of the double bond in the ring system on treatment with mineral acids, analogous to lanost-9(11)-en-3β-yl acetate.[6,9,10,20] Compounds such as lanost-7-en-3β-yl acetate,[11] euph-7-en-3β-yl acetate,[12] and triucall-7-en-3β-yl acetate[13] that contain the double bond between C(7) and C(8) are known to be readily converted with acids into compounds having the double bond at C(8)–C(9). Further, the fact that the isolated double bond can be hydrogenated under catalytic conditions parallels the behavior of lanost-9(11)-en-3β-ol, while lanost-7-en-3β-ol is resistant.

An observation that supported the view that the double bond in the ring system of abieslactone must be at C(9)–C(11) was secured by the oxidation of the 3α-methoxylanostene (XXIII) with chromic acid in acetic acid, when a yellow enedione (XXXII), λ_{max} 275 mμ (log ε 3·89), ν_{max} 1680 and 1674 cm^{-1}, and an enone (XXXIII), λ_{max} 245 mμ (log ε 4·10), ν_{max} 1677 and 1600 cm^{-1}, were formed. Since the enedione (XXXII) showed no signal corresponding to an olefinic proton, the double bond in this compound must be tetrasubstituted and accordingly was attributed to the

position C(8)–C(9). Furthermore the UV spectrum of the enedione (XXXII) is characteristic of those of Δ^8-7,11-diones in the steroid and triterpenoid series.[6] On the other hand the enone (XXXIII) showed a one-hydrogen doublet (J = 2·0 c/s) for an olefinic proton at τ 4·40 and its UV spectrum was similar to those of 3β-acetoxylanost-9(11)-en-12-one,[9] 3α-acetoxyarbor-9(11)-en-12-one,[14] and methyl 12-ketodavallate.[15] The ORD curve of the enone (XXXIII) depicted in Fig. 1 exhibited a strong negative multiple Cotton effect which was very similar to those of 3α-acetoxy-arbor-9(11)-en-12-one[14] and 3β-acetoxy-18α-olean-9(11)-en-12-one.[16]

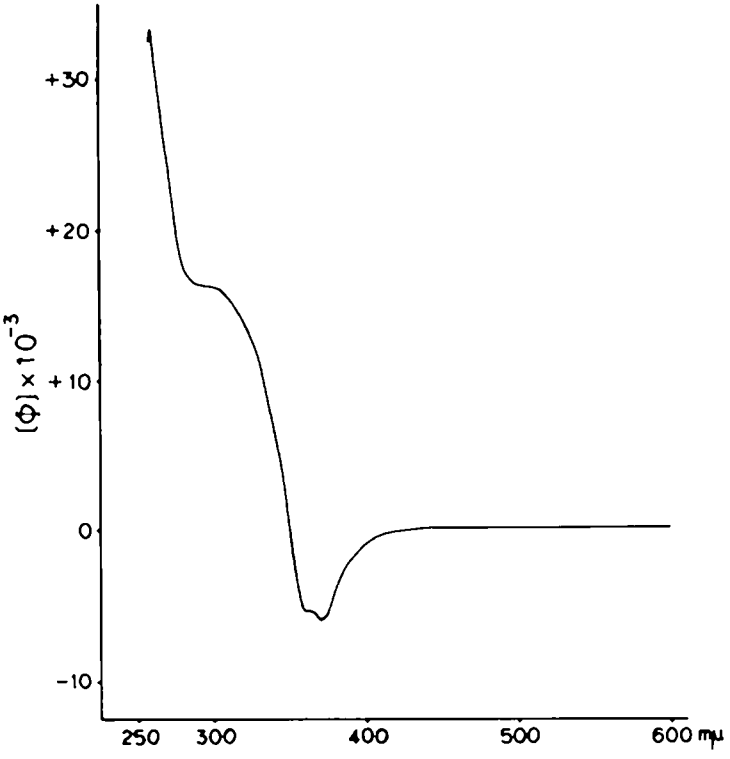
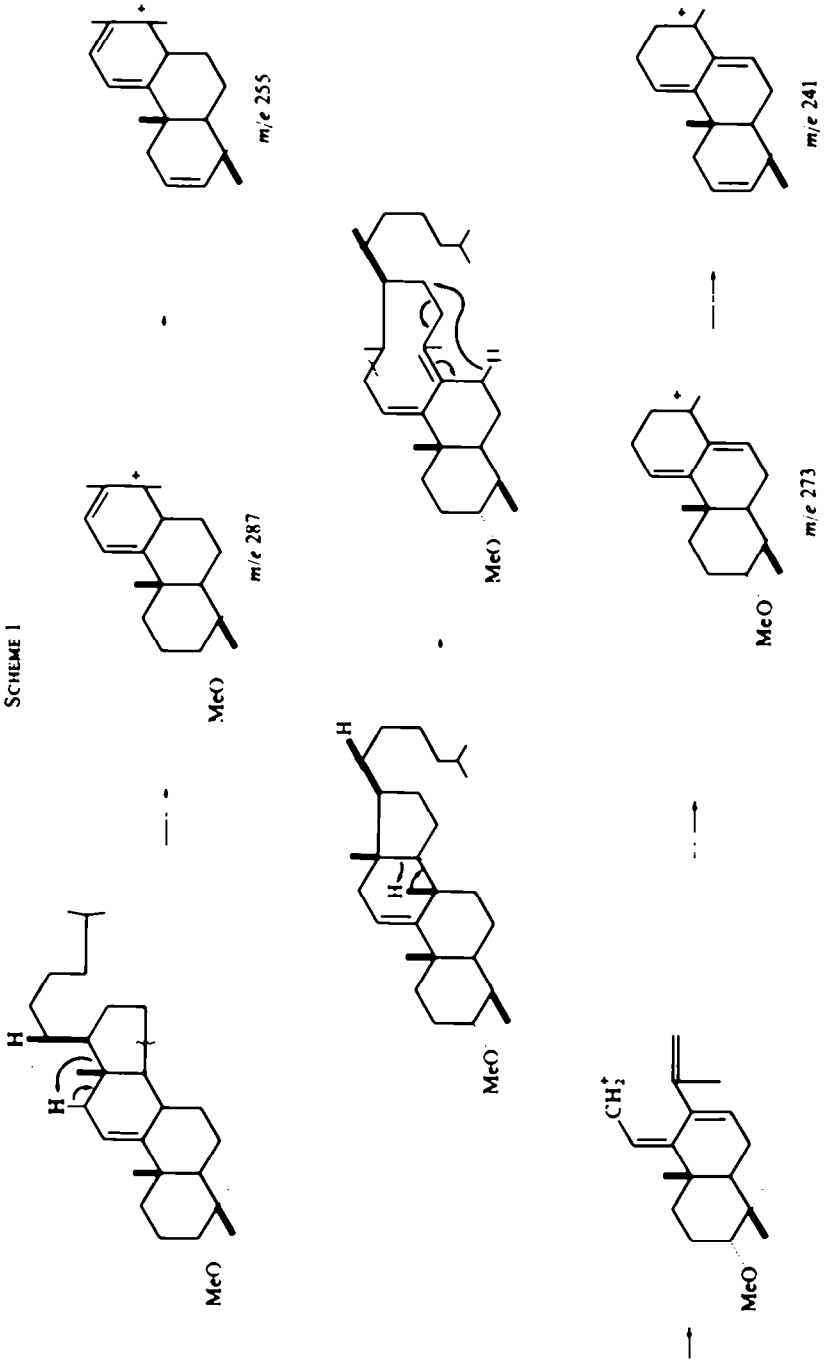


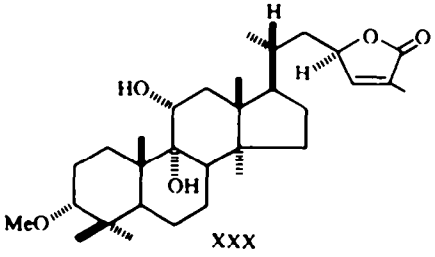
FIG. 1. ORD-curve of 3α-methoxylanost-9(11)-en-12-one (XXXIII) in dioxan.

The foregoing facts suggested that the enedione had the structure of 3α-methoxylanost-8-ene-7, 11-dione (XXXII) and the enone that of 3α-methoxylanost-9(11)-en-12-one (XXXIII). Additional evidence supporting the position of the double bond in abieslactone was provided by the mass spectrum of the 3α-methoxylanostene (XXIII). This exhibited the parent peak at *m/e* 442, two peaks corresponding to M·CH_3 and M CH_3·CH_2OH (*m/e* 427 and 395), and four fragment peaks at *m/e* 287, 273, 255, and 241. Occurrence of these four peaks in the mass spectrum of the methoxylanostene is analogous to the fragmentation pattern of arborene[14,15,17,18] that contains a double bond at C(9)–C(11). A plausible mechanism is shown in Scheme 1.

SCHEME 1



Proof for this inference has now been brought about by converting the methoxylanostene (XXIII) to lanost-9(11)-en-3-one. Hydrobromic acid hydrolysis of the methoxylanostene in boiling acetic anhydride–acetic acid in an atmosphere of carbon dioxide furnished, in addition to a compound that was presumably lanosta-2, 9(11)-diene (XXXIV), a lanosten-3α-yl acetate (XXXV) that was saponified with ethanolic potassium hydroxide to give a lanosten-3α-ol (XXXVI). Oxidation of this axial alcohol with chromic acid-pyridine complex afforded the ketone XXXVII, m.p. 121–122°, $[\alpha]_D$ +59·7° ($CHCl_3$).



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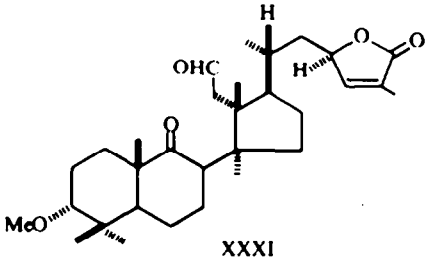
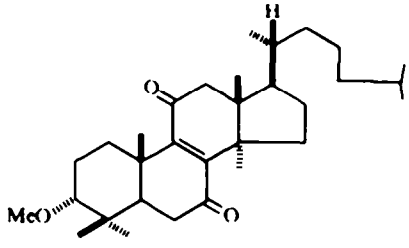
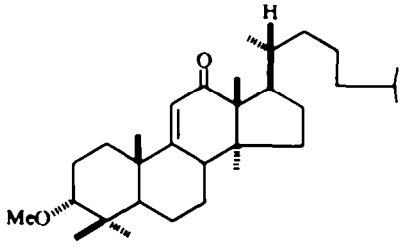


XXXI



XXXII



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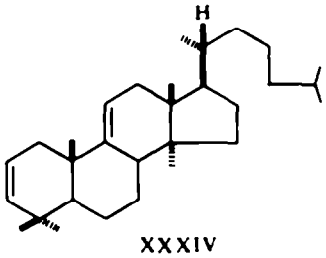
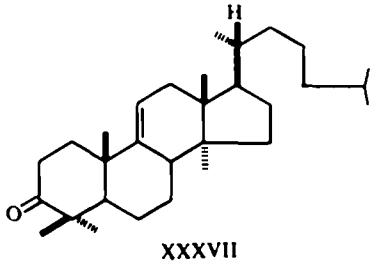
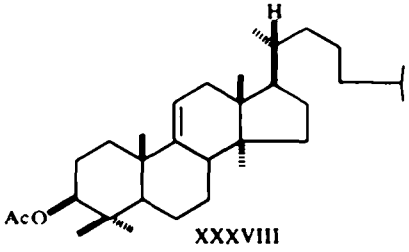


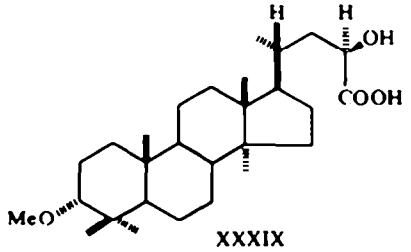
XXXIV



XXXVII



XXXVIII



XXXIX

As shown in Table 2, the m.p. of this compound was slightly higher than the m.ps given in the literature for lanost-9(11)-en-3-one (XXXVII).

TABLE 2

Compound	M.p.	$[\alpha]_D$	Ref.
XXXVII	121–122°	+59·7	
Lanost-9(11)-en-3-one	113–114°	+65°	19
	111–111·5°	+60·7	15

However, a mixed m.p. determination of our compound with an authentic sample showed no depression of the m.p. and the IR spectra and thin layer chromatograms of both samples were superimposable, so that identity of both samples was established beyond doubt. Further confirmation was provided by comparison of the m.p. and optical rotation of the compound obtained by sodium borohydride reduction of our lanostenone (XXXVII) and subsequent acetylation with those reported for lanost-9(11)-en-3β-yl acetate (XXXVIII). (Table 3).

TABLE 3

	M.p.	$[\alpha]_D$	Ref.
XXXVIII	171–172°	+84·3	
Lanost-9(11)-en-3β-yl acetate	171–172°	+87°	20
	170–171°	+81°	6
	170–172°	+85°	9
	177–178°	+83°	10

On the basis of the evidence thus accumulated, the structure and the stereochemistry of the 3α-methoxylanostene derived from abieslactone were established as represented by the formula XXIII. Finally, we must elucidate the configuration at C(23) before the entire stereochemistry of abieslactone is established.

On the basis of his measurement of the circular dichroism of abieslactone that showed a very weak positive peak at 249 mμ ($\theta = +306°$) for the $n \rightarrow \pi^*$ transition of the unsaturated lactone, Prof. G. Snatzke, Bonn University, West Germany, suggested that abieslactone probably has an R configuration at C(23).

More definite results were obtained by measuring the CD curves of the trisnorhydroxy-acid (V) and its dihydro derivative (XXXIX).

As shown in Fig. 2, the CD curves of these two compounds showed a weak trough at about 220 mμ and a strong positive peak at a shorter wavelength. If we compare these curves with that of L-(+)-lactic acid[21] that exhibited a positive peak at 213 mμ, it is clear that these trisnorhydroxy-acids (V and XXXIX) have an R configuration at C(23). If we rule out the highly improbable inversion at C(23) in the course of the permanganate oxidation of abieslactone to the trisnorhydroxy-acid (V), abieslactone

itself must have an R configuration at C(23), and the complete absolute configuration of abieslactone is represented as I.

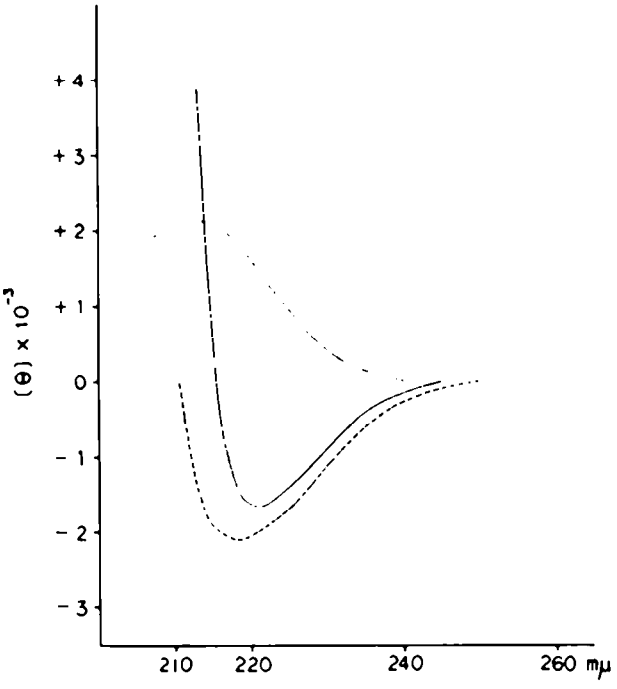


FIG. 2. CD-curves of V, XXXIX, and L-(+)-lactic acid in MeOH; ——, V; - · · , XXXIX; . . . . . , L-(+)-lactic acid.

Abieslactone was submitted to the U.S. Cancer Chemotherapy National Service Center, but found to be without significant effect on three different types of cancer. It was also submitted to Dr. D. Rosenthal, The Squibb Institute for Medical Research, New Brunswick, N.J., U.S.A., for antibiotic testing. It was found to be only mildly active against typical gram positive and gram negative organisms, and inactive against yeasts and fungi.

EXPERIMENTAL

M.ps are uncorrected, unless otherwise noted.

Specific rotations were measured in $CHCl_3$ soln. NMR spectra were measured in $CDCl_3$ soln on a Varian A-60 spectrometer using TMS as an internal reference.* Mass spectra were measured on a Hitachi mass spectrometer RMU-6D using an all-glass heated inlet system. Some IR and NMR spectra have been deposited with the Scientific Documentation Centre, Dunfermline, U.K.; their numbers are indicated as "(SDC No.)".

Isolation of abieslactone (I)

The dried bark of *Abies mariesii* Masters (12·3 kg) was chopped and extracted with EtOAc (50 l.) under reflux for 24 hr. The EtOAc extract was filtered, and the filtrate was concentrated to 10 l., decanted from resinous ppts, and again concentrated to 1·5 l. The crystalline mass formed on standing overnight was

* s = singlet, tr = triplet, m = multiplet, qu = quartet.

collected by filtration, and the filtrate was evaporated to 1 l. to give a further crop of crystals. The crystalline materials were combined and taken up in $CHCl_3$ (1 l.). The $CHCl_3$ soln was filtered from insoluble resinous materials and evaporated to give crystals that were washed with 200 ml of hot MeOH.

Crystallization from EtOAc afforded *abieslactone* (I) as colorless prisms (29·5 g), m.p. 252–253°, $[\alpha]_D^{20}$ −113° (*c*, 1·00). λ_{max}^{EtOH} 207·5 mμ (log ε 4·30). ν_{max}^{KBr} 1745, 1658, 1100, 838 cm^{-1} (SDC No. BWKG); $\nu_{max}^{CHCl_3}$ 1748 cm^{-1}; $\nu_{max}^{CS_2}$ 1767 cm^{-1}; ν_{max}^{Nujol} 1736 cm^{-1}. NMR (SDC No. BWLN): τ 8·90, 9·00, 9·06, 9·08 (six C-Me's), 8·10 (3H tr, J = 1·7 c/s, vinylic Me), 7·20 (1H narrow diffused tr, J = 1·8 c/s, equatorial H—C(—OMe)—), 6·73 (3H s, OMe), 5·03 (1H m, —CH—O), 4·48 (1H m, H—C=C—), and 3·00 (1H apparent quintet J = 1·7 c/s, —CH—CH=C(—CO)). Decoupling at 100 Mc showed that the 3·00 signal collapsed to a quartet when decoupled from 5·03, and to a doublet when decoupled from 8·10. Similarly, the 8·10 signal collapsed to a doublet when decoupled from either 3·00 or 5·03. The 5·03 signal collapsed to a broadened singlet when decoupled from the adjacent methylene at about τ 8·4 to which it is coupled by J = 9 c/s. The 4·48 signal collapsed to a sharp triplet, J = 3·5 c/s, when decoupled from the C-8 hydrogen at τ 7·61, and collapsed to a broadened singlet, J = ~1 c/s, when decoupled from the C-12 methylene at τ 7·81. ORD (*c*, 0·04348, in dioxan): $[\phi]_{440}$ −412°, $[\phi]_{300}$ −3070°, $[\phi]_{250}$ −11,300°, $[\phi]_{223}$ −27,200° (trough), $[\phi]_{210}$ −8240°. CD (*c*, 0·04348, in dioxan): $[\theta]_{300\ 235}$ 0°, $[\theta]_{214·5}$ −36,100° (trough), $[\theta]_{211}$ −30,100°. (Found: C, 79·56; H, 10·37; O, 10·30; OMe, 6·50. $C_{31}H_{48}O_3$ requires: C, 79·43; H, 10·32; O, 10·24; OMe, 6·62%). Mass spectrum: *m/e* 468 (M^+), 455 ($M^+ - CH_3$), 421 ($M^+ - CH_3 - CH_3OH$).

Titrimetric estimation of the lactone ring in abieslactone (I)

Abieslactone (46·50 mg) was refluxed with N/100 EtOH–KOH (F = 0·8464, 25·00 ml) for 30 min. After cooling, the soln was titrated with N/100 HCl (F = 1·0176) using phenolphthalein as an indicator. The consumed alkaline soln (10·97 ml) corresponded to one lactone ring in the molecule. Abieslactone gave positive Liebermann–Burchardt, Salkowski and Kariyone–Hashimoto tests, but a negative Legal test.

Dihydroabieslactone

Abieslactone I (200 mg) in THF (50 ml) was hydrogenated over 20% Pd·C (500 mg) at room temp for 1·5 hr. After one mole H_2 (10·3 ml) had been absorbed, H_2 uptake ceased. The catalyst was removed by filtration, and the filtrate was evaporated to give a solid mass (204 mg), which was dissolved in a mixture of hexane and benzene (1:1). The soln was applied to a column of neutral alumina (Woelm, grade I, 6 g), which was eluted with benzene. Evaporation of the eluate gave crystals (189 mg), m.p. 213–216° that on repeated crystallization from EtOH–benzene afforded *dihydroabieslactone* (II; 102 mg) as colorless prisms, m.p. 219–221°, $[\alpha]_D^{11}$ −15° (*c*, 0·99). ν_{max}^{KBr} 1770 and 1100 cm^{-1}, $\nu_{max}^{CHCl_3}$ 1759 cm^{-1}. NMR: τ 9·08, 9·06, 9·00, 8·96 (six C-Me's), 8·73 (3H doublet J = 6·5 c/s, CH_3—CH—CO), 7·18 (1H narrow diffused tr, J = 1·7 c/s, equatorial H—C(—OMe)—), 6·71 (3H s, OMe), 5·53 (1H broad m, —CH—O—), and 4·47 (1H m, H—C=C—). (Found: C, 78·95; H, 10·70. $C_{31}H_{50}O_3$ requires: C, 79·10; H, 10·71%).

Lithium aluminum hydride reduction of abieslactone (I)

A soln of LAH (50 mg) in dry THF (20 ml) was added to a soln of abieslactone (500 mg) in dry THF (100 ml). The mixture was stirred at room temp for 10 hr. A small amount of water was added, and the solvent was evaporated to dryness. The residue was acidified with dil H_2SO_4 and extracted with ether. The extract was washed with water and dried over Na_2SO_4. Removal of the ether gave a pasty residue (500 mg), which on chromatography on alumina (15 g) and elution with ether afforded, after crystallization from pet. ether (b.p. 50–60°), a crystalline product (151 mg), m.p. 125–128°. Rechromatography of this compound on alumina (5 g) and recrystallization from pet. ether–ether, furnished 3α-*methoxylanosta*-9(11), 24-*dien*-23ξ, 27-*diol* (III) (127 mg) as needles, m.p. 134–136°. $\nu_{max}^{CHCl_3}$ 3360, 1654 cm^{-1}. The product exhibited a yellow color with tetranitromethane. (Found: C, 78·67; H, 11·30. $C_{31}H_{52}O_3$ requires: C, 78·76; H, 11·09%).

Treatment of the diol (III) *with p-nitrobenzoyl chloride*

A mixture of III (100 mg) and *p*-nitrobenzoyl chloride (100 mg) in dry pyridine (2 ml) was kept at room temp for 24 hr, then poured into water, and the resulting ppt was collected by filtration. The solid was dissolved in ether, and the ether extract was washed with 10% Na_2CO_3 and water, and then dried over Na_2SO_4. Removal of the ether gave a solid residue that was recrystallized four times from MeOH–benzene to afford *the di-p-nitrobenzoate* (148 mg) as colorless needles, m.p. 166–168°. (Found: C, 69·99; H, 7·91. $C_{45}H_{58}O_9N_2$ requires: C, 70·10; H, 7·58%).

Tetrahydroabieslactone (IV)

Abieslactone (502 mg) was dissolved in EtOAc (200 ml) and AcOH (20 ml), PtO_2 (117 mg) was added, and the mixture was hydrogenated at room temp and atm press. One mole of H_2 was absorbed in about 2 hr and a second mole was absorbed after about 30 hr. The catalyst was filtered off, and the soln taken to dryness to yield colorless crystals, m.p. 226–231°. The product was crystallized alternately from CH_2Cl_2–MeOH and from hexane several times and sublimed at 220°/0·015 mm Hg to give IV (3α-*methoxylanostan*-27, 23*R*-*olide*), m.p. 230–231° (cor.), $[\alpha]_D^{24}$ +71° (*c*, 1·3). UV end absorption: λ_{max}^{EtOH} 196. No color with tetranitromethane. ν_{max}^{KBr} 1766 cm^{-1} (SDC No. BWKD), $\nu_{max}^{CHCl_3}$ 1762 cm^{-1}, $\nu_{max}^{CCl_4}$ 1785 cm^{-1}. NMR (SDC No. BWLK): τ 5·57 (1H, broad m, –CH(O)C=O). (Found: C, 78·65; H, 11·22; MeO, 6·71. $C_{31}H_{52}O_3$ requires: C, 78·76; H, 11·09; MeO, 6·56%).

Potassium permanganate oxidation of abieslactone (I)

A soln of $KMnO_4$ (717 mg) in AcOH (10 ml) at 50° was added dropwise to a soln of abieslactone (438 mg) in hot AcOH (100 ml). After the mixture was kept at room temp for 8 hr, aqueous $NaHSO_3$ was added in small portions to destroy the excess of $KMnO_4$. The solvent was evaporated *in vacuo* and the residue was dissolved in ether that was extracted with 5% NaOH (100 ml). Acidification of the alkaline extract with dil HCl gave the white ppt that was taken up in ether. The ether extract was washed with water, dried over Na_2SO_4, and evaporated to give a residue (389 mg) that on chromatography on silica gel (10 g) afforded, after elution with $CHCl_3$, colorless crystals (108 mg). It was recrystallized from benzene–acetone to give *the trisnor hydroxy acid* (V) (25,26,27-*trisnor*-3α-*methoxy*-23*R*-*hydroxylanost*-9(11)-*en*-24-*oic acid*) (81 mg), as colorless needles, m.p. 225–227°, $[\alpha]_D^{28}$ +58·0° (*c*, 0·89). λ_{max}^{MeOH} 206 mμ (ε 724). $\nu_{max}^{CHCl_3}$ 3360, 1690 cm^{-1}. ORD (*c*, 0·03804, in MeOH): $[\phi]_{400}$ +1086°, $[\phi]_{250}$ +4610°, $[\phi]_{227}$ +9710°, $[\phi]_{220}$ +17,500°, $[\phi]_{212}$ +35,040° (peak). CD (*c*, 0·03804, in MeOH): $[\theta]_{245}$ 0°, $[\theta]_{221}$ −1650° (trough), $[\theta]_{215.5}$ 0°, $[\theta]_{213}$ +38,800°. (Found: C, 75·23; H, 10·25. $C_{28}H_{46}O_4$ requires: C, 75·29; H, 10·38%).

The trisnor-hydroxy acid methyl ester (VI)

To a soln of V (93 mg) in ether (2 ml), an ether soln of diazomethane was added. After the evolution of N_2 subsided, the solvent was evaporated to dryness *in vacuo*. The resulting solid was chromatographed on alumina (3 g). The compound was eluted with ether and recrystallized from petroleum ether–CH_2Cl_2 to give VI (*methyl* 25,26,27-*trisnor*-3α-*methoxy*-23*R*-*hydroxylanost*-9(11)-*en*-24-*oate*) (86 mg), as colorless prisms, m.p. 197–198°, $[\alpha]_D^{28}$ +53·8° (*c*, 0·81). $\nu_{max}^{CHCl_3}$ 3550, 1725 cm^{-1}. NMR: τ 8·93, 9·07, 9·12, 9·17, 9·30 (six C-Me's), 7·15 (1H diffused tr, J = 1·8 c/s, equatorial H–C(OMe)), 6·69 (3H s, OMe), 6·33 (3H s, COOMe), 6·25 (1H m, CH_2–CH(OH)COOMe) and 4·66 (1H m, H–C=C). (Found: C, 75·57; H, 10·53. $C_{29}H_{48}O_4$ requires: C, 75·60; H, 10·50%).

The acetate of V

To a soln of V (120 mg) in dry pyridine (3 ml) was added Ac_2O (3 ml), the mixture kept at room temp overnight, and the solvents evaporated to dryness *in vacuo*. The resulting residue was dissolved in $CHCl_3$ and chromatographed over silica gel (5 g). Elution with $CHCl_3$ yielded a solid, which on crystallization from MeOH gave *the acetate* VII (25,26,27-*trisnor*-3α-*methoxy*-23*R*-*acetoxylanost*-9(11)-*en*-24-*oic acid*) (87 mg) as colorless prisms, m.p. 252–254°, $[\alpha]_D^{28}$ +33·0° (*c*, 0·74). $\nu_{max}^{CHCl_3}$ 1730, 1710 cm^{-1}. NMR: τ 8·90, 9·06, 9·13, 9·21, 9·28 (six C-Me's), 7·98 (3H s, OAc), 7·15 (1H diffused tr, J = 1·8 c/s, equatorial H–C(OMe)),

6·70 (3H s, OMe), 5·01 (1H broad m, H–C–OAc) and 4·65 (1H m, H–C=C–). (Found: C, 73·27; H, 10·04. $C_{30}H_{48}O_5$ requires: C, 73·07; H, 10·15%).

Methyl ester acetate of V

(a) The ester VI (70 mg) in dry pyridine (1 ml) was treated with Ac_2O (1 ml) in the same manner as before. Chromatography of the residue on alumina (3 g) gave, after elution with benzene, crystals, which on recrystallization from n-hexane furnished *the corresponding acetate* VIII (*methyl* 25,26,27-*trisnor*-3α-*methoxy*-23R-*acetoxylanost*-9(11)-*en*-24-*oate*), (67 mg) as colorless prisms, m.p. 160–161°, $[\alpha]_D^{28}$ +28·0° (*c*, 1·13). $\nu_{max}^{CHCl_3}$ 1730 cm^{-1} (COOMe and OAc). NMR: τ 8·90, 9·06, 9·13, 9·21, 9·28 (six C–Me's), 7·98 (3H s, OAc), 7·16 (1H diffused tr, J = 1·8 c/s, equatorial H–C–OMe), 6·70 (3H s, OMe), 6·33 (3H s, COOMe), 5·01 (1H broad m, H–C–OAc) and 4·63 (1H m, H–C=C–). (Found: C, 74·05; H, 10·19. $C_{31}H_{50}O_5$ requires: C, 74·06; H, 10·03%).

(b) The acetate VII (56 mg) was methylated with diazomethane as described in the preparation of VI. Elution of the product with benzene from a column of alumina (3 g) gave, after crystallization from n-hexane, *the methyl ester acetate* VIII (50 mg), as colorless prisms, m.p. 160–161°. The compound was identical with that obtained by procedure (a) by a mixed m.p. determination and comparison of their IR spectra.

Alkaline hydrolysis of abieslactone (I)

A soln of abieslactone (500 mg) in N/4 EtOH–KOH (20 ml) was refluxed for 1·5 hr, then concentrated to about 5 ml *in vacuo*. After dilution with water, the alkaline mixture was acidified with dil HCl. The product was extracted with ether, which was washed with water, and dried over Na_2SO_4. Removal of the ether gave a residue (500 mg), which was dissolved in $CHCl_3$ and adsorbed on a column of silica gel (20 g). Elution with $CHCl_3$ gave a colorless solid mass that on crystallization from pet. ether (b.p. 50–60°) furnished *the keto acid* IX (3α-*methoxy*-23-*ketolanost*-9(11)-*en*-27-*oic acid*) (481 mg), as prisms, m.p. 133–134·5°, $[\alpha]_D^{20}$ −72·3° (*c*, 1·01) λ_{max}^{EtOH} 276 mμ (log ε 1·72), ν_{max}^{KBr} 1713, $\nu_{max}^{CHCl_3}$ 1710 cm^{-1}. NMR: τ 8·73, 8·84, 8·95, 9·00, 9·05, 9·09 (seven C–Me's), 7·17 (1H diffused tr, J = 2·0 c/s, equatorial H–C–OMe), 6·71 (3H s, OMe) and 4·48 (1H m, H–C=C–). (Found: C, 76·44; H, 10·31; O, 13·19. $C_{31}H_{50}O_4$ requires: C, 76·50; H, 10·36; O, 13·15%). The mass spectrum of IX exhibited peaks identical with those of abieslactone (I).

The keto acid methyl ester (X)

The keto acid IX (500 mg) was treated with an ether soln (10 ml) of diazomethane prepared from nitrosomethylurea (1 g) in essentially the same manner as described in the preparation of VI. The substance thus obtained was chromatographed on alumina (20 g). Benzene eluated a colorless solid (483 mg) that on crystallization from MeOH furnished X (*methyl* 3α-*methoxy*-23-*ketolanost*-9(11)-*en*-27-*oate*) as needles, m.p. 72–74°, $[\alpha]_D^{21}$ −19·7° (*c*, 0·97). $\nu_{max}^{CHCl_3}$ 1738, 1715 cm^{-1}. NMR: τ 8·76, 8·87, 8·95, 8·99, 9·03, 9·07 (seven C–Me's), 7·18 (1H diffused tr, J = 2·0 c/s, equatorial H–C–OMe), 6·70 (3H s, OMe), 6·30 (3H s, COOMe) and 4·45 (1H m, H–C=C–). (Found: C, 76·92; H, 10·36; O, 12·56. $C_{32}H_{52}O_4$ requires: C, 76·75; H, 10·47; O, 12·78%).

The 2,4-*dinitrophenylhydrazone of the keto ester* (X)

A soln of X (50 mg), 2,4-dinitrophenylhydrazine (22 mg), and two drops of conc HCl in EtOH (3 ml) was refluxed for 20 min. The crystalline ppt formed on cooling was collected by filtration and washed with EtOH. Recrystallization from EtOH afforded *the hydrazone*, as yellow needles, m.p. 163–164°. (Found: C, 67·02; H, 8·25; N, 8·48. $C_{38}H_{56}O_7N_4$ requires: C, 67·03; H, 8·29; N, 8·23%).

Treatment of the keto acid (IX) *with boiling acetic anhydride*

The keto acid IX (100 mg) in Ac_2O (5 ml) was heated under reflux for 2·5 hr. The solvent was evaporated *in vacuo*, and the residue crystallized from EtOAc to give fine prisms (21 mg), m.p. 252–254°, $[\alpha]_D^{11}$ −116°

(*c*, 1·07). The IR spectrum of this compound was superimposable on that of authentic abieslactone (I). (Found: C, 79·51; H, 10·30. $C_{31}H_{48}O_3$ requires: C, 79·43; H, 10·32%). From the mother liquor, the starting keto-acid (31 mg) was recovered unchanged.

Catalytic hydrogenation of keto ester (X)

A hydrogenation bomb was loaded with X (1·8 g), PtO_2 (494 mg), EtOAc (40 ml), and AcOH (40 ml). This mixture was reduced for 17 hr at 150° under 1700 lb/in² press of H_2. The catalyst was filtered off, and the product extracted as usual. This product (1·677 g) was absorbed onto a column of alumina (Woelm, neutral, activity II; 50 g) and left overnight. Chromatography then yielded two main fractions and one minor component. Pet. ether–benzene eluted crystalline *saturated deoxo ester* XI (*methyl 3α-methoxylanostan-27-oate*, 560 mg), m.p. 61–62°. Elution with ether–EtOH–AcOH (5:3:2), followed by extraction, yielded IV, (501 mg), identical with an authentic sample, and *the saturated deoxo acid* XII (*3α-methoxylanostan-27-oic acid*, 82 mg) which was colorless with tetranitromethane. No trace of desired demethoxy derivatives was detected.

The deoxo ester XI was saponified by refluxing for 3 hr with 1·5 N MeOH–NaOH (50 ml) and extracted as usual. The resulting XII was recrystallized several times from MeOH, m.p. 90–93° (cor.), $[\alpha]_D^{24}$ +47° (*c*, 1·2). UV end absorption: $\varepsilon_{203\,m\mu}^{EtOH}$ 250. $\nu_{max}^{melted\ film}$ 1705 cm^{-1} (SDC No. BWKE). NMR (SDC No. BWLL): τ 7·21 (1H narrow diffused tr, equatorial H–C–OMe), 6·71 (3H s, OMe). (Found: C, 78·39; H, 11·31; MeO, 6·52. $C_{31}H_{54}O_3$ requires: C, 78·42; H, 11·47; MeO, 6·54%).

Lithium aluminum hydride reduction of the keto ester (X)

A mixture of X (300 mg) and LAH (80 mg) in dry ether (30 ml) was stirred at room temp for 12 hr. After addition of a small amount of water to destroy the excess of LAH, the mixture was acidified with dil H_2SO_4. The ether layer was washed with water, dried over Na_2SO_4, and evaporated. The residue (281 mg) was chromatographed on alumina (10 g). Elution with benzene yielded a solid that on crystallization from n-hexane–acetone furnished XIII (*3α-methoxylanost-9(11)-en-23ξ, 27-diol*) as colorless prisms, m.p. 161–163°, $[\alpha]_D^{27}$ −41·2° (*c*, 0·80). $\nu_{max}^{CHCl_3}$ 3350 cm^{-1}. NMR: τ 8·97, 9·00, 9·05, 9·08 (seven C–Me's), 7·20 (3H complicated broad m, overlapping of a proton geminal to the O-Me group with two protons arising from two OH groups. Signals corresponding to two OH protons were removed by addition of D_2O while a narrow diffused triplet at 7·20 having J = 2·0 c/s remained), 6·72 (3H s, OMe), 6·45 (3H broad m, –CH–OH and $-CH_2-OH$) and 4·47 (1H m, H–C=C–). (Found: C, 78·55; H, 11·49. $C_{31}H_{54}O_3$ requires: C, 78·42; H, 11·47%).

Tosylation of the diol (XIII)

A soln of XIII (300 mg) and toluene-*p*-sulfonyl chloride (250 mg) in dry pyridine (20 ml) was allowed to stand at room temp for 2 days. Removal of pyridine *in vacuo* followed by addition of cold water gave a solid, which was dissolved in ether. The ether soln was washed successively with dil HCl, water, dil Na_2CO_3 and water, dried over Na_2SO_4 and then evaporated to dryness. Recrystallization of the residue (269 mg) from acetone gave *the diol monotosylate* XIV (197 mg), as colorless needles, m.p. 126–128°. (Found: C, 72·08; H, 9·89. $C_{38}H_{60}O_5S$ requires: C, 72·56; H, 9·61%).

Formation of the oxide (XV) *from the monotosylate* (XIV)

(a) To a soln of XIV (85 mg) in dry ether (10 ml), a soln of LAH (10 mg) in dry ether (5 ml) was added, and the mixture kept at room temp for 24 hr. Isolation of the product in the manner as described in the preparation of XIII afforded a substance (60 mg) that was dissolved in n-hexane and applied to a column of alumina (5 g). Elution with n-hexane gave a solid (43 mg) that was crystallized from acetone to furnish *the oxide* XV (*3α-methoxylanost-9(11)-en-23ξ, 27-oxide*) as colorless prisms, m.p. 114–116°, $[\alpha]_D^{27}$ +15·6° (*c*, 0·42). $\nu_{max}^{CHCl_3}$ 1097, 1085 cm^{-1} (absence of OH band). NMR: τ 8·91, 8·95, 9·00, 9·05, 9·07, 9·12 (seven C–Me's), 7·18 (1H narrow diffused tr, J = 1·8 c/s, equatorial H–C–OMe), 6·71 (3H s OMe, and 1H m, –CH–O–), 5·93 and 6·18 (2H, q, J = 7·5 c/s, $-CH-CH_2-O-$), 4·45 (1H m, H–C=C–) (Found: C, 81·50; H, 11·67; O, 6·78. $C_{31}H_{52}O_2$ requires: C, 81·52; H, 11·48; O, 7·01%).

(b) A soln of XIV (186 mg) in $CHCl_3$ was applied to a column of silica gel (20 g). Elution with $CHCl_3$ afforded *the oxide* XV, m.p. 114–116°, identical in all respects with the compounds obtained in (a).

Lithium aluminum hydride reduction of tetrahydroabieslactone (IV)

To a suspension of LAH (2·45 g) in dry ethylene glycol dimethyl ether (30 ml) was added IV (0·774 g) in warm ethylene glycol dimethyl ether (30 ml). The mixture was stirred for 1 hr, and then refluxed for 1 hr. Excess hydride was then destroyed with EtOAc, and the mixture extracted as usual to yield a crystalline product (0·749 g). This product was carefully chromatographed on alumina (Woelm, neutral, activity II, 20 g). Benzene–ether and ether–EtOH eluted *the homogeneous diol* XVI (*3α-methoxylanostan-23ξ,27 diol*, 0·694 g), m.p. 151·5–152°. This was recrystallized several times from a small amount of cold MeOH for analysis, m.p. 152·5–153·5° (cor.), $[\alpha]_D^{23}$ + 54° (*c*, 1·4). (Found: C, 78·08; H, 11·86; MeO, 6·58. $C_{31}H_{56}O_3$ requires: C, 78·09; H, 11·84; MeO, 6·51%). The IR spectrum (SDC No. BWKC) was as expected.

The diol XVI was converted to its di-3,5-dinitrobenzoate in the usual way with 3,5-dinitrobenzoyl chloride and pyridine. Recrystallization several times from $CHCl_3$–EtOH and CH_2Cl_2–hexane yielded pale yellow fine needles, m.p. 177·5–179° (cor.). (Found: C, 62·53; H, 7·01. $C_{45}H_{60}O_{13}N_4$ requires: C, 62·49; H, 6·99%). The IR spectrum (SDC No. BWKB) was as expected.

Conversion of the diol (XVI) *to the oxide* (XVII)

Compound XVI (1·03 g) was converted to a glassy tosylate by treatment with *p*-toluensulfonyl chloride and pyridine. The ester in ethylene glycol dimethyl ether (25 ml) was slowly added to a soln of LAH (5·75 g) in the same solvent (25 ml). After stirring for 1 hr, the soln was refluxed for 3 hr, the excess hydride destroyed with EtOAc, and the mixture extracted in the usual way to yield a pale yellow oil (0·926 g). This was carefully chromatographed on alumina (Woelm, neutral, activity II, 50 g). Pet ether–benzene mixtures eluted oily methoxyhydrocarbons (292 mg) from which no pure compound could be isolated. Benzene–ether eluted a crystalline oxide (368 mg). Benzene–MeOH eluted hydromethoxy derivatives (209 mg) that were an oily mixture from which no pure crystalline component could be isolated.

The *oxide* XVII (*3α-methoxylanostan-23, 27-oxide*) obtained above was crystallized several times from a small volume of MeOH, m.p. 116·5–118·5° (cor.). ν_{max}^{KBr} 1098 cm^{-1} (strong, —O—) (SDC No. BWKA).

NMR (SDC No. BWLJ): τ 7·22 (1H narrow diffused tr, equatorial H·  , 6·71 (3H s OMe, and 1H m, ), 6·20 and 5·99 (2H qu, J = 8 c/s, each peak further split to J = 1 c/s, —O—CH$_2$—CH).

(Found: C, 81·14; H, 11·86. $C_{31}H_{54}O_2$ requires: C, 81·16; H, 11·87%).

Thioketal of the keto-ester (X)

BF_3–ether complex (2 ml) was added to a soln of X (1·549 g) and ethanedithiol (2 ml) in dry ether (10 ml) with ice cooling, and the mixture was allowed to stand at room temp for 15 hr. The colorless crystals (1·286 g), m.p. 143–147°, which separated were collected on a filter and washed with pet. ether. The filtrate was washed with dil Na_2CO_3 and water, dried over Na_2SO_4 and then evaporated to dryness. The resulting solid (477 mg) was chromatographed on neutral alumina (Woelm, neutral, activity II, 20 g). Elution with ether afforded an additional crop (398 mg) of the compound, m.p. 142–147°. Recrystallization of the combined products from EtOH gave *the thioketal* XVIII (*methyl 3α-methoxy-23, 23-ethylenedithiolanost-9(11)-en-27-oate*) as prisms, m.p. 151–152°, $[\alpha]_D^{28}$ + 27·0° (*c*, 0·91). $\nu_{max}^{CHCl_3}$ 1727 cm^{-1}. NMR: τ 8·73, 8·86, 8·94, 9·01, 9·06, 9·12, 9·26, 9·31 (seven C–Me's), 7·20 (1H diffused tr, J = 1·8 c/s, equatorial H· ), 6·76 (4H s, —S—CH$_2$—CH$_2$—S—), 6·70 (3H s, OMe), 6·33 (3H s, COOMe), and 4·78 (1H m, H– ). (Found: C, 70·55; H, 9·72. $C_{34}H_{56}O_3S_2$ requires: C, 70·78; H, 9·78%).

Desulfurization of the thioketal (XVIII)

W_2–Raney Ni (prepared from 20 g of Raney alloy) was added to a soln of XVIII (910 mg) in EtOH (50 ml), and the mixture was boiled for 10 hr. After cooling, the catalyst was removed by filtration, and the filtrate was evaporated *in vacuo* to give a residue (758 mg), which was dissolved in n-hexane and chromatographed on a column of alumina (30 g). Elution with benzene afforded a colorless mass (723 mg), which was crystallized from MeOH to give XIX (*methyl 3α-methoxylanost-9(11)-en-27-oate*), as prisms, m.p. 89–90°,

$[\alpha]_D^{25}$ +45·6° (*c*, 1·05). $\nu_{max}^{CHCl_3}$ 1729 cm^{-1}. NMR: τ 8·82, 8·92, 8·94, 9·02, 9·07, 9·14, 9·27, 9·37 (seven C–Me's), 7·20 (1H diffused tr, J = 1·8 c/s, equatorial H—C—OMe), 6·71 (3H s, OMe), 6·34 (3H s, COOMe) and 4·78 (1H m, H—C=C—). (Found: C, 79·24; H, 11·21. $C_{32}H_{54}O_3$ requires: C, 78·96; H, 11·18%). Mass spectrum: *m/e* 486 (M^+).

Lithium aluminum hydride reduction of the deoxo-ester XIX

A soln of LAH (100 mg) in dry ether (10 ml) was added with stirring to a soln of XIX (700 mg) in dry ether (50 ml), and the mixture was allowed to stand at room temp for 15 hr. Treatment of the product in the manner described for the preparation of XIII gave a product (686 mg), that was chromatographed on alumina (20 g). Elution with benzene–ether (1:1) afforded colorless crystals (669 mg) that on crystallization from n-hexane furnished XX (3α-*methoxylanost*-9(11)-*en*-27-*ol*), as prisms, m.p. 139·5–140·5°, $[\alpha]_D^{28}$ +37·5° (*c*, 1·04). $\nu_{max}^{CHCl_3}$ 3600 cm^{-1}. NMR: τ 8·93, 9·01, 9·07, 9·13, 9·26, 9·35 (seven C–Me's), 7·20 (1H diffused tr, J = 1·8 c/s, equatorial H—C—OMe), 6·70 (3H s, OMe), 6·55 (2H d, J = 5·8 c/s, –CH–CH_2–OH) and 4·77 (1H m, H—C=C). (Found: C, 80·89; H, 12·04. $C_{31}H_{52}O_2$ requires: C, 81·16; H, 11·87%).

Tosylation of the alcohol XX

A mixture of XX (625 mg) and toluene-*p*-sulfonyl chloride (250 mg) in dry pyridine (5 ml) was allowed to stand at room temp for 2 days and then poured into cold water. The usual work up gave the product (753 mg), which on crystallization from MeOH afforded XXI, as colorless prisms, m.p. 90–91°, $[\alpha]_D^{28}$ +34·6° (*c*, 0·94). $\nu_{max}^{CHCl_3}$ 1600 (aromatic C=C), 1360 and 1170 (–SO_2–O–) cm^{-1}. (Found: C, 74·56; H, 9·98; S, 5·02. $C_{38}H_{60}O_4S$ requires: C, 74·46; H, 9·87; S, 5·23%).

Conversion of the tosylate XXI *to* 3α-*methoxylanost*-9(11)-*ene* (XXIII)

(a) A soln of XXI (200 mg) in CCl_4 was applied to a column of alumina (10 g). Elution with CCl_4 gave XXII (56 mg), which exhibited a strong band at $\nu_{max}^{CCl_4}$ 888 cm^{-1} (terminal methylene group) in the IR spectrum. Further elution with ether recovered the unchanged tosylate (108 mg). A soln of XXII (50 mg) in EtOAc (20 ml) was hydrogenated over Pd–C (prepared from 1·5 ml of 3% $PdCl_2$) for 12 hr. After working up in the usual manner, the product (50 mg) was chromatographed on alumina (3 g). Elution with pet. ether (b.p. 50–60°) afforded crystals (41 mg), which on recrystallization from MeOH–CH_2Cl_2 gave XXIII as prisms, m.p. 93·94°, $[\alpha]_D^{29}$ +42·6° (*c*, 1·01). ν_{max}^{KBr} 1632 cm^{-1} (–C=C–). NMR: τ 8·93, 9·07, 9·09, 9·13, 9·18, 9·26, 9·35 (eight C–Me's), 7·18 (1H diffused tr, J = 2·3 c/s, equatorial H—C—OMe), 6·70 (3H s, OMe), 4·75 (1H m, H—C=C). (Found: C, 84·35; H, 12·19. $C_{31}H_{54}O$ requires: C, 84·09; H, 12·29%).

(b) A soln of XXI (500 mg) in dry ether (30 ml) was added to a stirred soln of LAH (150 mg) in dry ether (20 ml). After standing at room temp for 12 hr, the reaction mixture was treated with a small amount of water and dil H_2SO_4 to destroy the excess hydride. The ethereal soln was washed with water, dried over Na_2SO_4, and then evaporated to dryness. Chromatography of the residual solid (448 mg) on alumina (15 g) and elution with n-hexane gave colorless crystals (431 mg) that on recrystallizations from MeOH–CH_2Cl_2 gave XXIII (371 mg), as colorless prisms, m.p. 93–94°, $[\alpha]_D^{28}$ +42·1° (*c*, 1·04). This compound was identical in all respects with that prepared in (a). (Found: C, 84·35; H, 12·30. $C_{31}H_{54}O$ requires: C, 84·09; H, 12·29%). Mass spectrum: *m/e* 442 (M^+), 427, 395, 287, 273, 255, 241.

3α-*Methoxylanostane* (XXIV)

Compound XXIII (165 mg) in AcOH (60 ml) was hydrogenated over PtO_2 (150 mg) under atm press at 90° for 20 hr. The residue, after removal of the catalyst and solvent, was chromatographed in n-hexane on alumina (10 g). Elution with n-hexane gave a colorless solid which on recrystallization from MeOH—CH_2Cl_2 furnished XXIV (156 mg), as prisms, m.p. 112–113°, $[\alpha]_D^{20}$ –2·0° (*c*, 1·01). ν_{max}^{KBr} 1107 cm^{-1}. NMR: τ 9·09, 9·15, 9·19, 9·23 (eight C–Me's), 7·20 (1H diffused tr, J = 2·3 c/s, equatorial H—C—OMe), 6·70 (3H s, OMe).

This compound gave no color reaction with tetranitromethane. (Found: C, 83·86; H, 12·35. $C_{31}H_{56}O$ requires: C, 83·71; H, 12·69%).

Lanostan-3α-yl acetate (XXV)

To a soln of XXIV (100 mg) in AcOH (5 ml) 47% HBr (0·6 ml) and Ac_2O (4 ml) were added under a stream of CO_2. After boiling for 1 hr, the mixture was poured into cold water, and the resulting ppt was extracted with ether. The ether extract was washed with aqueous Na_2CO_3 and water, dried over Na_2SO_4, and evaporated to dryness. Chromatography of the residue (104 mg) on alumina (5 g) gave, on elution with n-hexane, an oily unsaturated hydrocarbon (17 mg) and unchanged XXIV (57 mg). Further elution with n-hexane–benzene (3:1) afforded a solid (17 mg), m.p. 153–157°, which, on recrystallization from MeOH—CH_2Cl_2 gave XXV, as colorless prisms, m.p. 158–159°, $[\alpha]_D^{24}$ −28·9° (*c*, 0·83). ν_{max}^{KBr} 1745, 1240 cm^{-1}. NMR: τ 9·09, 9·10, 9·18, 9·23 (eight C–Me's), 7·93 (3H s, OAc), and 5·36 (1H tr, J = 2·7 c/s, equatorial H—C—OAc). (Found: C, 81·51; H, 11·78. $C_{32}H_{56}O_2$ requires: C, 81·29; H, 11·94%).

Lanostan-3α-ol (XXVI)

A soln of XXV (85 mg) in N/5 EtOH–KOH (10 ml) was refluxed for 1·5 hr. After the usual working up, the crude product (65 mg) was chromatographed on a column of alumina (Woelm, neutral, activity II, 3 g) and eluted with benzene to give a solid. Recrystallization from MeOH–CH_2Cl_2 gave XXVI (59 mg), as prisms, m.p. 164–165°, $[\alpha]_D^{23}$ +21·5° (*c*, 1·01). $\nu_{max}^{CHCl_3}$ 3600 cm^{-1}. NMR: τ 9·05, 9·12, 9·17, 9·22 (eight C–Me's) and 6·55 (1H diffused tr, J = 2·5 c/s, equatorial H—C—OH). (Found: C, 83·36; H, 12·45. $C_{30}H_{54}O$ requires: C, 83·65; H, 12·64%).

Lanostan-3-one (XXVII)

To a soln of XXVI (53 mg) in pyridine (1 ml), a mixture of CrO_3 (50 mg) and pyridine (1·5 ml) was added with cooling. The mixture was allowed to stand at room temp for 2 hr, then diluted with water, and the resulting ppt extracted with ether, washed with dil HCl and water, and then dried over Na_2SO_4. Evaporation of the ether gave a crude product (51 mg), which was chromatographed on alumina (3 g). The column was eluted with n-hexane–benzene (10:1) to yield a solid which on recrystallization from MeOH–ether furnished prisms of XXVII (41 mg), m.p. 133–134°, $[\alpha]_D^{21}$ +28·4° (*c*, 0·88). ν_{max}^{KBr} 1707 cm^{-1}. ORD (*c*, 1·002, in dioxan): $[\alpha]_{700}$ +13°, $[\alpha]_{589}$ +27°, $[\alpha]_{361}$ +54°, $[\alpha]_{331}$ −42° (trough), $[\alpha]_{279}$ +469°, $[\alpha]_{273}$ +459°, $[\alpha]_{256}$ +519°. NMR: τ 8·92, 8·94, 9·09, 9·21 (eight C–Me's). (Found: C, 84·30; H, 12·26. Calc. for $C_{30}H_{52}O$: C, 84·04; H, 12·23%). This showed no depression in mixture m.p. with lanostan-3-one prepared from lanosterol by the known method.[6,7] The IR, NMR, ORD, and TLC of both samples were identical.

Lanostan-3β-ol (XXVIII)

A mixture of XXVII prepared from abieslactone (30 mg) and $NaBH_4$ (7 mg) in EtOH (2·5 ml) was kept at room temp for 2 hr and then a small amount of AcOH was added to destroy the excess of $NaBH_4$. Evaporation of the solvent *in vacuo* followed by the addition of water precipitated the crude product, which was extracted with ether. The ether extract was washed with water and dried over Na_2SO_4. After evaporation of the ether, the residue (30 mg) was chromatographed on alumina (2 g). Elution with n-hexane–benzene (1:1) afforded a solid that on recrystallization from MeOH–CH_2Cl_2 gave XXVIII (23 mg), as prisms, m.p. 180–181°, $[\alpha]_D^{23}$ +31·0° (*c*, 1·00). $\nu_{max}^{CHCl_3}$ 3600 cm^{-1}. NMR: τ 9·04, 9·10, 9·21, 9·25 (eight C–Me's), and 6·80 (1H qu, J_{AX} = 9·0 c/s J_{BX} = 5·5 c/s, axial H—C—OH). (Found: C, 83·45; H, 12·59. $C_{30}H_{54}O$ requires: C, 83·63; H, 12·64%). There was no depression in mixed m.p. with an authentic sample of lanostan-3β-ol. The IR and NMR spectra and TLC of the samples were identical.

3β-Methoxylanost-8-ene

Metallic K (15 mg) was added to a soln of lanost-8-en-3β-ol (200 mg) in dry benzene (20 mg), and the mixture was refluxed with stirring in a stream of N_2 for 5 hr. After cooling, MeI (1 ml) was added and the soln again refluxed with stirring for 4 hr. A small amount of MeOH was added to destroy the excess K and the reaction mixture washed with water, and dried over Na_2SO_4. Evaporation of the benzene gave the product (200 mg), which was dissolved in n-hexane and chromatographed on a column of alumina (10 g). Elution with n-hexane gave a solid (155 mg), which on crystallization from MeOH–CH_2Cl_2 gave

3β-*methoxylanost*-8-*ene* as colorless prisms, m.p. 130–131°, $[\alpha]_D^{29}$ +77·4° (*c* 0·98). $\nu_{max}^{CHCl_3}$ 1094 cm^{-1}. NMR: τ 9·01, 9·08, 9·12, 9·17, 9·19, 9·31 (eight C–Me's), 7·31 (1H qu, J_{AX} = 10·0 c/s J_{BX} = 4·0 c/s, axial H—C—OMe) and 6·63 (3H s, OMe). (Found: C, 84·23; H, 12·17. $C_{31}H_{54}O$ requires: C, 84·09; H, 12·29%).

3β-*Methoxytirucall*-8-*ene*

Tirucall-8-en-3β-ol (156 mg) was methylated in the same manner as described for the preparation of 3β-methoxylanost-8-ene, and the resulting product (150 mg) was chromatographed on alumina (8 g). Elution with n-hexane gave a solid (81 mg) that on recrystallization from MeOH–CH_2Cl_2 afforded 3β-*methoxytirucall*-8-*ene* as colorless prisms, m.p. 94–95°, $[\alpha]_D^{27}$ +13·4° (*c*, 1·12). $\nu_{max}^{CHCl_3}$ 1095 cm^{-1}. NMR: τ 9·01, 9·05, 9·08, 9·13, 9·18, 9·21, 9·25 (eight C–Me's), 7·31 (1H qu, J_{AX} = 10·0 c/s J_{BX} = 4·0 c/s, axial H—C—OMe), and 6·63 (3H s, OMe). (Found: C, 84·24; H, 12·33. $C_{31}H_{54}O$ requires: C, 84·09; H, 12·29%).

Chromic acid oxidation of abieslactone (I)

A soln of CrO_3 (230 mg) in 90% AcOH (10 ml) was added slowly with stirring into a soln of I (250 mg) in hot AcOH (40 ml) at 55°. Stirring was continued at 60° for 4·5 hr, and then the solvent was evaporated *in vacuo*. The residue was dissolved in ether, washed with aqueous Na_2CO_3 and water, and dried over Na_2SO_4. Evaporation of the ether gave a yellow solid (264 mg) that was chromatographed on silica gel (15 g). Elution with $CHCl_3$ yielded yellow crystals (86 mg) that on recrystallization from MeOH afforded XXIX (3α-*methoxy*-7, 11-*diketolanosta*-8, 24-*dien*-27, 23R-*olide*), as yellow plates, m.p. 215–216°, $[\alpha]_D^{18}$ +3·2° (*c*, 0·93). λ_{max}^{EtOH} 274 mμ (log ε 3·84). $\nu_{max}^{CHCl_3}$ 1752, 1678, 1100 cm^{-1}. NMR: τ 8·71, 8·75, 8·85, 9·07, 9·18 (6 C–Me's), 8·10 (3H tr, *J* = 1·7 c/s, vinylic Me), 7·14 (1H diffused tr, *J* ≈ 3·0 c/s, equatorial H—C—OMe), 6·72 (3H s, OMe), 5·06 (1H m, —CH—O—) and 3·02 (1H quintet *J* ≈ 1·7 c/s, —O—CH—CH=C(CO)(CH₃)).

(Found: C, 74·68; H, 9·04. $C_{31}H_{44}O_5$ requires: C, 74·96; H, 8·93%).

Osmium tetroxide oxidation of abieslactone (I)

Abieslactone (835 mg) and OsO_4 (1 g) were dissolved in diethylene glycol dimethyl ether (200 ml) and the soln was left for 2 weeks at room temp in the dark. The osmate ester was decomposed by saturating the soln with H_2S,[22] and the resulting suspension filtered through a column containing celite, active carbon, and powdered silver. The column was eluted with $CHCl_3$–EtOH, and the eluates were evaporated. The residue was recrystallized several times from MeOH and from CH_2Cl_2–hexane to give the colorless crystalline XXX (3α-*methoxy*-9α, 11α-*dihydroxylanost*-24-*en*-27, 23-*olide*), m.p. 241–245° (cor.), colorless with tetranitromethane, λ_{max}^{EtOH} 210 mμ (ε 13,180). The IR (SDC No. BWKF) was as expected, NMR (SDC No. BWLM): τ 7·65 and 8·30 (2H sharp s, OH, absent when D_2O added), 5·95 (1H broad m, axial H—C—OH). (Found: C, 74·24; H, 10·09. $C_{31}H_{50}O_5$ requires: C, 74·06; H, 10·03%).

Periodic acid oxidation of the diol XXX

To a soln of XXX (563 mg) in ethylene glycol dimethyl ether (10 ml) was added periodic acid (1·0 g) in water (2 ml). The soln was left 3 days in a refrigerator and then poured into water (100 ml) and extracted with toluene (100 ml). The toluene layer was washed twice with water (50 ml). The water extracts were washed serially with fresh toluene (50 ml). Arsenious acid (0·44 g) and $NaHCO_3$ (2·0 g) were then added to the combined water extracts. The soln was distilled, and the distillate (100 ml) gave absolutely no ppt with dimethyldihydroresorcinol or with 2,4-dinitrophenylhydrazone. It gave a negative test for acetone by the salicylaldehyde method.[23]

The combined toluene layers were washed with $NaHCO_3$ soln, dried, and evaporated to yield crude crystalline XXXI (9,11-*seco*-3α-*methoxy*-9,11-*dioxolanost*-24-*en*-27, 23R-*olide*, 442 mg), whose IR spec-

trum showed that the conjugated lactone and OMe groups were still present, the OH groups were gone, and new CO bands were present at 1712 and 1727 cm^{-1} (CCl_4). A pure product could not be isolated on chromatography on alumina due to alumina-catalyzed condensations of the aldehyde group.

Treatment of XXIII *with hydrogen chloride*

A soln of XXIII (50 mg) in AcOH (10 ml) containing 1% of HCl gas was refluxed for 2 hr. After concentration to 3 ml *in vacuo*, the soln was poured into water, and the resulting ppt was extracted with ether. The extract was washed with dil Na_2CO_3 soln and water, dried over Na_2SO_4, and then evaporated to dryness. The residue was chromatographed on alumina (2 g). Elution with n-hexane gave a solid that on crystallization from MeOH-CH_2Cl_2 gave colorless crystals, m.p. 93–94°. The product was identical in all respects with XXIII.

Chromic acid oxidation of 3α-*methoxylanost*-9(11)-*ene*

Compound XXIII (200 mg) in AcOH (10 ml) was treated with CrO_3 (220 mg) in 90% AcOH (5 ml) at 60° as described for the oxydation of I. The yellow product (211 mg) thus obtained was dissolved in pet. ether (b.p. 50–60°) and chromatographed on alumina (10 g). Pet. ether–benzene (4:1) eluated a yellow product (14 mg), which on crystallization from MeOH afforded XXXII as yellow plates, m.p. 109–110°, $[\alpha]_D^{27}$ +41·8° (*c*, 0·39). λ_{max}^{EtOH} 275 mμ (log ε 3·89). $\nu_{max}^{CHCl_3}$ 1678 cm^{-1}; ν_{max}^{KBr} 1674, 1680 cm^{-1}. NMR: τ 8·69, 8·83, 9·07, 9·09, 9·20 (8 C-Me's), 7·13 (1H diffused tr, J = 3·0 c/s, equatorial H—C(OMe)) and 6·70 (3H s, OMe). Mass spectrum: *m/e* 470 (M^+), ($C_{31}H_{50}O_3$: mol wt 470·71).

Further elution of the column with pet. ether–benzene (1:1) gave a colorless crystalline product that on several recrystallizations from MeOH gave XXXIII (27 mg), as prisms, m.p. 141–142°, $[\alpha]_D^{28}$ +60·4° (*c*, 0·92). λ_{max}^{EtOH} 245 mμ (log ε 4·10). $\nu_{max}^{CHCl_3}$ 1600, 1673 cm^{-1}; ν_{max}^{KBr} 1600, 1677 cm^{-1}. ORD (*c*, 0·002521, in dioxan): $[\alpha]_{700}$ +46°, $[\alpha]_{589\ 490}$ +54°, $[\alpha]_{370}$ −1240° (trough), $[\alpha]_{360}$ −1160°, $[\alpha]_{291}$ +3570°, $[\alpha]_{260}$ +7280°. NMR: τ 8·83, 9·00, 9·05, 9·09, 9·18, 9·25 (8 C-Me's), 7·16 (1H diffused tr, J = 2·3 c/s, equatorial H—C(OMe)), 6·70 (3H s, OMe) and 4·40 (1H d, J = 2·0 c/s, bearing the axial H in the γ-position, HC(CO)—C(CO)=CH–CO). (Found: C, 81·33; H, 11·56. $C_{31}H_{52}O_2$ requires: C, 81·52; H, 11·48%).

Lanost-9(11)-*en*-3α-*yl acetate* (XXXV)

To a soln of XXIII (100 mg) in AcOH (5 ml), 47% HBr (0·6 ml) and Ac_2O (4 ml) were added in an atm of CO_2 and the soln boiled for 1 hr. After working up in the usual manner, the crude product (102 mg) was chromatographed on alumina (5 g). Elution with n-hexane gave colorless crystals (18 mg), which was rechromatographed on alumina (1 g), and the compound eluted with n-hexane was crystallized from n-hexane several times to give *an unsaturated hydrocarbon* XXXIV, as needles, m.p. 109–111°. No band at 1100 cm^{-1} in the IR spectrum that was present in that of XXIII. NMR: τ 8·92, 9·09, 9·18, 9·25, 9·33 (8 C-Me's) and 4·45–4·75 (3H complicated broad m, overlapping of the protons on >C=C(H)– and H—C(OAc)—C(H)=). This compound was assigned *lanosta*-2,9(11)-*diene* from the above data (Found: C, 87·41; H, 12·03. $C_{30}H_{50}$ requires: C, 87·73; H, 12·27%).

Further elution of the column with n-hexane followed by n-hexane–benzene (5:1) gave, both unchanged XXIII (54 mg) and colorless crystals (21 mg). Several recrystallizations of the latter compound from MeOH-CH_2Cl_2 gave XXXV, as prisms, m.p. 136–137°, $[\alpha]_D^{20}$ +36·1° (*c*, 1·30). ν_{max}^{KBr} 1734, 1240 cm^{-1}. NMR: τ 8·91, 8·99, 9·13, 9·17, 9·20, 9·33 (8 C-Me's), 7·93 (3H s, OAc), 5·32 (1H diffused tr, J = 2·5 c/s, equatorial H—C(OAc)—) and 4·75 (1H m, H—C=C—). (Found: C, 81·51; H, 11·58. $C_{32}H_{54}O_2$ requires: C, 81·64; H, 11·56%).

Lanost-9(11)-en-3α-ol (XXXVI)

A soln of XXXV (68 mg) in N/5 EtOH–KOH (10 ml) was refluxed for 1·5 hr. After working up in the usual manner, the resulting product (63 mg) was chromatographed on alumina (3 g). Elution with ether gave crystals (56 mg), m.p. 136–140°. Recrystallization from MeOH–CH_2Cl_2 gave *lanost-9(11)-en-3α-ol* XXXVI, as prisms, m.p. 142–143°, $[\alpha]_D^{20}$ +59·0° (*c*, 0·61). $\nu_{max}^{CHCl_3}$ 3580 cm^{-1}. NMR: τ 8·95, 9·06, 9·10, 9·13, 9·20, 9·37 (8 C–Me's), 6·57 (1H diffused tr, J = 2·5 c/s, equatorial H—C—OH) and 4·75 (1H m, H C=C).

(Found: C, 84·24; H, 12·21. $C_{30}H_{52}O$ requires: C, 84·04; H, 12·23%).

Lanost-9(11)-en-3-one (XXXVII)

Compound XXXVI (96 mg) in dry pyridine (1 ml) was oxidized with CrO_3 (100 mg) in dry pyridine (3 ml) as described for XXVII. The crude product (94 mg) was purified by chromatography on alumina (5 g) and eluted with n-hexane–benzene (5:1) to furnish colorless crystals (71 mg), m.p. 117–122°. Recrystallization from MeOH gave XXXVII as prisms, m.p. 121–122°, $[\alpha]_D^{13}$ +59·7° (*c*, 0·85). ν_{max}^{KBr} 1712 cm^{-1}. NMR: τ 8·76, 8·86, 8·91, 9·07, 9·17, 9·25, 9·32 (8 C–Me's), and 4·70 (1H m, H C=C). ORD (*c*, 1·717, in dioxan): $[\alpha]_{589}$ +34°, $[\alpha]_{362}$ +122°, $[\alpha]_{316}$ −52°, $[\alpha]_{270}$ +839°, $[\alpha]_{254}$ +984°. (Found: C, 84·45; H, 11·83. $C_{30}H_{50}O$ requires: C, 84·44; H, 11·81%). Although the m.p. of the XXXVII was slightly higher than that previously reported, there was no depression in mixed m.p. with an authentic specimen of lanost-9(11)-en-3-one, m.p. 113–114°. The IR spectra, ORD curves, and TLC of the two samples were identical.

Lanost-9(11)-en-3β-yl acetate (XXXVIII)

Compound XXXVII (60 mg) in EtOH (4 ml) was treated with $NaBH_4$ (20 mg) at room temp. The crude product (60 mg) was chromatographed on alumina (3 g). Elution with n-hexane–benzene (1:2) gave lanost-9(11)-en-3β-ol (54 mg), m.p. 160–165°. This alcohol was acetylated with Ac_2O (1 ml) and pyridine (1 ml), and the resulting product (56 mg) was chromatographed on alumina (3 g). Elution with n-hexane–benzene (5:1) yielded colorless crystals that on recrystallization from MeOH–CH_2Cl_2 gave XXXVIII (47 mg), as prisms, m.p. 171–172°, $[\alpha]_D^{21}$ +84·3° (*c*, 0·75). ν_{max}^{KBr} 1735, 1240 cm^{-1}. NMR: τ 8·92, 9·08, 9·11, 9·12, 9·17, 9·25, 9·35 (8 C Me's), 7·95 (3H s, OAc), 5·45 (1H qu J_{AX} = 9·5 c/s J_{BX} = 4·5 c/s, axial H—C—OAc) and 4·75 (1H m, H C=C). Mass spectrum: *m/e* 470 (M^+), ($C_{32}H_{54}O_2$: mol wt 470·75).

25,26,27-*Trisnor-3α-methoxylanostan-24-oic acid* (XXXIX)

A soln of V (46 mg) in AcOH (20 ml) was hydrogenated over PtO_2 (50 mg) at 90° for 120 hr. During hydrogenation, fresh PtO_2 (20 mg) each was added in every 24 hr. After filtration, the soln was evaporated. The residue was treated with 5% EtOH–KOH (5 ml) under reflux for 30 min. The alkaline soln was concentrated *in vacuo* and poured into water. Acidification of this soln with dil HCl gave a deposit, which was filtered, washed with water, and dried. Chromatography of the solid (45 mg) on silica gel afforded a product, (11 mg), m.p. 162–181° from the first eluate. Further elution with $CHCl_3$ gave the unchanged acid IV (32 mg). The first product was further purified twice by column chromatography as described to furnish a product, m.p. 168–171° (8 mg). Recrystallization from hexane–CH_2Cl_2 afforded *trisnorhydroxy acid* XXXIX (25,26,27-*trisnor-3α-methoxylanost-9(11)-en-24-oic acid*, 5 mg), as prisms, m.p. 170–171°, which gave no color with tetranitromethane, $[\alpha]_D^{28}$ +27·4° (*c*, 0·61). ν_{max}^{Nujol} 3360, 1962 cm^{-1}. ORD (*c*, 0·04178 in MeOH): $[\phi]_{400}$ +644°; $[\phi]_{250}$ +2040°; $[\phi]_{215}$ +9235°; $[\phi]_{210}$ +11,600°: CD (*c*, 0·04178 in MeOH): $[\theta]_{250}$ 0°; $[\theta]_{218}$ −2090° (trough); $[\theta]_{210.5}$ 0°. (Found: C, 74·93; H, 10·81. $C_{28}H_{48}O_4$ requires: C, 74·95; H, 10·78%).

ORD and CD of L-(+)-lactic acid

This optically active acid was commercially available. ORD (*c*, 0·05502 in MeOH); $[\phi]_{400}$ +41°; $[\phi]_{226.5}$ +1080° (peak); $[\phi]_{205}$ −1860°. CD (*c*, 0·05502 in MeOH): $[\theta]_{240}$ 0°; $[\theta]_{213}$ +2130° (peak); $[\theta]_{207}$ +1870°.

Acknowledgements - The authors are grateful to Professor D. H. R. Barton, Imperial College of Technology, London, England, for a generous gift of lanost-9(11)-en-3-one; to Professor G. Snatzke, Bonn University,

West Germany, and to Dr. K. Kuriyama, Shionogi & Co., Ltd., Osaka, Japan, for measuring the ORD and CD curves; and to Dr. D. P. Hollis, Varian Associates, for the 100 Mc decoupled NMR spectrum of abieslactone.

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