217. *Steroids. Part I. 4α-Methylergostane.*

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Methylation of ergosta-7,22-dien-3-one gives the 4α-methyl derivative (Ia), higher methylation products, and a bis-steroid. 4α-Methylergostane is obtained from the dienone (Ia) by standard procedures—through the 8(14)-en-3β-ol (IId) and the saturated ketone (Va), and through 4α-methylergosta-7,22-diene.

Methylation of cholestan-3-one, with methyl iodide and potassium t-butoxide in t-butyl alcohol, gives 2α-methylcholestan-3-one [1] whereas, under the same conditions, cholest-7-en-3-one yields the 4α-methyl derivative.[2] Advantage has been taken of the latter reaction to prepare a number of 4α-methyl compounds in the ergostane series.

Ergosta-7,22-dien-3-one [3] was prepared by oxidation of the corresponding alcohol with chromium trioxide in pyridine. When excess of the oxidising agent was destroyed with methanol a considerable amount of dimethyl ketal was formed. Acid hydrolysis of the ketal gave a high yield of the required ketone. Treatment of this ketone with one molar equivalent of methyl iodide in t-butyl alcohol containing potassium t-butoxide afforded 4α-methylergosta-7,22-dien-3-one (Ia), characterised as its oxime. With excess of methyl iodide the product was a mixture of at least six components, as shown by thin-layer chromatography, from which the 4α-methyl ketone was readily separated. A second component of this mixture was a bis-steroid, $C_{57}H_{88}O \pm CH_2$, the oxygen function of which is present in a six-membered ring ketone (strong infrared absorption at 1709 cm.$^{-1}$).

Table 1.

Molecular-rotation data for steriods methylated in ring A.

Compound	$[M]_D$ alcohol	$[M]_D$ acetate	Δ_1	Ref.
4α-Methylcholest-7-en-3β-ol (lophenol)	+20°	+124°	+104°	*a*
4α-Methylstigmasta-7,24(28)-dien-3β-ol (citrostadienol)	+102	+202	+100	*b*
4α-Methylergosta-7,22-dien-3β-ol (Id)	−111	+5	+116	
4α-Methylcholest-8(14)-en-3β-ol	+76	+181	+105	*a*
4α-Methylstigmast-8(14)-en-3β-ol	+98	+193	+95	*c*
4α-Methylergost-8(14)-en-3β-ol (IId)	+25	+109	+84	
2α-Methylcholestan-3β-ol	+32	−147	−179	*d*
4α-Methylcholestan-3β-ol	+109	+186	+77	*a*
4α-Methylstigmastan-3β-ol	+120	+184	+64	*c*
4α-Methylergostan-3β-ol (Vd)	+54	+128	+74	

a, Djerassi, Krakower, Lemin, Liu, Mills, and Villotti, *J. Amer. Chem. Soc.*, 1958, **80**, 6284. *b*, Weizmann and Mazur, *J. Org. Chem.*, 1958, **23**, 832. *c*, Mazur, Weizmann, and Sondheimer, *J. Amer. Chem. Soc.*, 1958, **80**, 6293. *d*, Ref. 1.

The structure and stereochemistry of the monomethyl ketone (Ia) follow: (i) by analogy with previous work [2] in the cholestane series; (ii) from the similarity between its rotatory dispersion curve (*a*, +62 *) and those for other 4α-methyl-5α*H*-7-en-3-ones (*a*, +59) and the corresponding nonmethylated ketones, (*a* +63); [4] and (iii) from the molecular-rotation data shown in Table 1. The changes in molecular rotation on acetylation of the 3β-ol (Id) and its di- and tetrahydro-derivatives (IId and Vd) (see below) are in good agreement with the values for analogous compounds in the cholestane and stigmastane series, and quite different from the value for a 2α-methyl-sterol.

Reduction of the ketone (Ia) with sodium borohydride, lithium aluminium hydride,

* The lower extremum could not be measured and this amplitude is a minimum value. For the definition of the molecular amplitude, *a*, see ref. 4.

[1] Mazur and Sondheimer, *J. Amer. Chem. Soc.*, 1958, **80**, 5220.
[2] Mazur and Sondheimer, *J. Amer. Chem. Soc.*, 1958, **80**, 6296; see also Sondheimer, Klibansky, Haddad, Summers, and Klyne, *J.*, 1961, 767; Bucourt, *Bull. Soc. chim. France*, 1963, 1265.
[3] Barton and Cox, *J.*, 1948, 1354.
[4] Djerassi and Klyne, *J.*, 1962, 4942.

or lithium tri-t-butoxyaluminium hydride [5] gave mixtures of epimeric alcohols that were separated by chromatography on silica gel. The first alcohol eluted (12—20% of the mixture), which did not form an ethanol-insoluble digitonide, showed a molecular rotation change of −48° on acetylation and is assigned the 3α(*ax*)-OH structure (Ib), while the major component showed a corresponding molecular rotation change of +116° and is assigned the 3β(*eq*)-OH structure (Id). Mixed, saturated ethanolic solutions of the latter compound and digitonin slowly deposited a digitonide from which the equatorial alcohol could be recovered. The formation of such a high proportion (12%) of axial epimer with lithium tri-t-butoxyaluminium hydride is surprising in view of the reported stereospecificity of this bulky reagent.[6]

The infrared spectra of the alcohols (Ib and Id) and the acetates (Ic and Ie) show characteristic differences of the type previously observed for steroids [7] and triterpenes.[8] It is interesting to note that while the 4-methyl-alcohols resemble the triterpenes in their spectra, their acetates resemble the steroids (Table 2).

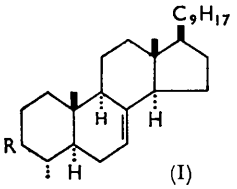
TABLE 2.

Infrared spectra (cm.$^{-1}$) of 3-hydroxy- and 3-acetoxy-steroids and triterpenes.

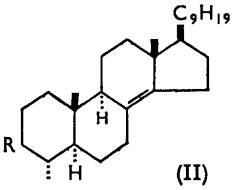
	ax-OH	*eq*-OH	*ax*-OAc	*eq*-OAc
Steroids [7]	996—1004	1035—1040	1016—1020 1240 (complex) *	1023—1029 1240 (simple) ‡
4α-Methyl-steroids	1070	1055	1017—1020 1240 (complex) †	1036 1240 (simple) ‡
Triterpenes [8]	1063—1069	1025—1040	1033—1035 1240 (simple) ‡	1024—1025 1240 (simple) ‡

* Usually 3 bands. † 3 Bands. ‡ Symmetrical singlet.

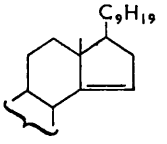
When the dienyl acetate (Ie), in acetic acid solution, was hydrogenated over platinum 4α-methylergost-8(14)-en-3β-yl acetate (IIe) was obtained. In the presence of hydrochloric acid a second mole of hydrogen was absorbed slowly to yield 4α-methylergostan-3β-yl acetate (Ve). The equilibrium 8(14)-ene (IIe) ⇌ 14-ene (IIIe) does not lie far to

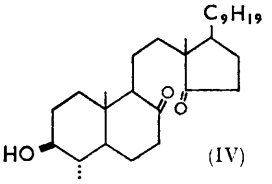


(I)

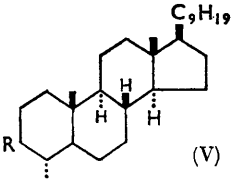


(II)

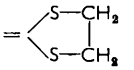

(III)



(IV)



(V)

a, R = O; b, R = H, α-OH; c, R = H, α-OAc; d, R = H, β-OH; e, R = H, β-OAc; f, R = H_2; g, R = 

the right since treatment of the 8(14)-enyl acetate (IIe) with hydrogen chloride in chloroform followed by hydrogenation of the product in neutral solution gave a mixture (*ca.* 2 : 1)

[5] Brown and McFarlin, *J. Amer. Chem. Soc.*, 1956, **78**, 252; 1958, **80**, 5372, 5377.
[6] Fajkos, *Chem. listy*, 1958, **52**, 2134; Wheeler and Mateos, *Canad. J. Chem.*, 1958, **36**, 1431; Wheeler and Huffman, *Experientia*, 1960, **16**, 516.
[7] Barton, *Experientia*, 1950, **6**, 316; Jones, Humphries, Herling, and Dobriner, *J. Amer. Chem. Soc.*, 1951, **73**, 3215; Cole, Jones, and Dobriner, *ibid.*, 1952, **74**, 5571; Jones and Herling, *ibid.*, 1956, **78**, 1152; Jones and Roberts, *ibid.*, 1958, **80**, 6121.
[8] Allsop, Cole, White, and Willix, *J.*, 1956, 4868.

of the saturated acetate (Ve) and starting material. The position of the double bond in the dihydro-compound (IIe) was confirmed by the method of Castells, Meakins, and Swindells [9]—successive treatment with osmium tetroxide, lithium aluminium hydride, and lead tetra-acetate, without isolation of the intermediates—and the infrared spectrum of the product then showed strong bands at 1736 (5-membered ring ketone) and 1712 cm.$^{-1}$ (6-membered ring ketone) due to the presence of the diketone (IV).

Wolff–Kishner reduction of 4α-methylergostan-3-one (Va) gave a high proportion of azine and only a low yield of 4α-methylergostane (Vf). The saturated hydrocarbon prepared in this way was difficult to purify and was best obtained by hydrogenation of 4α-methylergosta-7,22-diene (If) in the presence of hydrochloric acid. The diene (If) itself was prepared by Raney-nickel desulphurisation of the ethylene dithioketal (Ig) or by Wolff–Kishner reducion of the keto-diene (Ia).

Experimental

Rotations were determined for chloroform solutions at 18—22°, ultraviolet spectra for ethanol solutions, and infrared spectra for potassium bromide discs, unless otherwise indicated. M. p.s were determined in capillaries sealed at 10^{-2} mm. Light petroleum refers to the fraction b. p. 60—80°. Column-chromatographic separations were followed on thin layers (0·25 mm.) of alumina G or silica gel G (Merck) with the same solvent system as in the column. The thin-layer chromatograms were sprayed with chlorosulphonic acid–acetic acid (1 : 2), heated (5 min.) at 120°, and viewed in ultraviolet light. Samples for analysis were dried (24 hr.) at 78°/10^{-2} mm.

Ergosta-7,22-dien-3-one.—(*a*) 5α-Dihydroergosterol (5 g.) was left overnight at room temperature with chromium trioxide in pyridine and the product, isolated through chloroform, was chromatographed on alumina (80 g.). Elution with light petroleum–benzene (1 : 1) and crystallisation from chloroform–methanol yielded ergosta-7,22-dien-3-one (3·2 g.) as plates, m. p. 184—185° (open capillary), 194—195° (evacuated capillary), $[\alpha]_D$ +1 ± 2° (*c* 0·75) (lit.,[3] m. p. 184·5°, $[\alpha]_D$ +2°), $\lambda_{max.}$ 206 (ε 5000) and 210 mμ (ε 4500), $\nu_{max.}$ 1715 cm.$^{-1}$ (Found: C, 84·6; H, 10·7. Calc. for $C_{28}H_{44}O$: C, 84·8; H, 11·2%). Further elution of the column, with chloroform, gave starting material (1·2 g.)

In a similar experiment, methanol (10 ml.) was added to the reaction mixture immediately before the work-up. The crude product, isolated through ether, was chromatographed on alumina (500 g.). Elution with light petroleum (2·5 l.) removed an oil (30 mg.) which was discarded. Further elution with the same solvent (2 l.) and crystallisation from chloroform–methanol afforded 3,3-*dimethoxyergosta-7,22-diene* (950 mg.) as matted needles, m. p. 112·5—113°, $[\alpha]_D$ −19° (*c* 0·72), $\nu_{max.}$ 2825 cm.$^{-1}$ (C–H stretch in OMe) (Found: C, 81·2; H, 11·7. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·4%). Elution with light petroleum–benzene (1 : 1) gave the required ketone (2·4 g.).

(*b*) 3,3-Dimethoxyergosta-7,22-diene (100 mg.) in acetic acid (25 ml.) was stirred (2 hr.) at room temperature with concentrated hydrochloric acid (1 ml.). The mixture was diluted with water, and the precipitate crystallised from chloroform–methanol to yield the free ketone (80 mg.), m. p. and mixed m. p. 183—185° (open capillary), $[\alpha]_D$ +1° (*c* 0·76).

Methylation of Ergosta-7,22-dien-3-one.—(*a*) To a boiling solution of the keto-diene (5 g.) in benzene (100 ml.) was added potassium t-butoxide (from 1 g. of potassium) in t-butyl alcohol (85 ml.). Methyl iodide (1 ml.) in benzene (10 ml.) was then added dropwise (during *ca.* 10 min.) and the reaction mixture refluxed for a further 30 min. The crude product was isolated through ether and chromatographed on alumina (300 g.). Elution with light petroleum–benzene (3 : 1; 500 ml.) gave a mixture (1·1 g.) that showed 4 spots on a thin-layer chromatogram. Further elution with the same solvent mixture (2 l.) afforded 4α-*methylergosta-7,22-dien-3-one* (1·8 g.), m. p. 184—185° (needles from chloroform–methanol), $[\alpha]_D$ −24° (*c* 0·86), $\lambda_{max.}$ 206 (ε 4600) and 210 mμ (ε 4300); $\nu_{max.}$ 1715 cm.$^{-1}$ (Found: C, 84·7; H, 11·2. $C_{29}H_{46}O$ requires C, 84·8; H, 11·3%). The 4α-methyl ketone, when treated with hydroxylamine hydrochloride and pyridine in refluxing ethanol, gave an *oxime*, m. p. 235—236° (needles from methanol), $[\alpha]_D$ −30° (*c* 1·10) (Found: C, 82·7; H, 11·3; N, 3·0. $C_{29}H_{47}NO$ requires C, 81·8; H, 11·1; N, 3·3%). Continued elution of the column, again with the same solvent mixture (400 ml.),

[9] Castells, Meakins, and Swindells, *J.*, 1962, 2917.

yielded a fraction (1·6 g.) containing mainly starting material (as shown by thin-layer chromatography).

(*b*) Methyl iodide (25 ml.) in benzene (100 ml.) was added (during *ca.* 30 min.) to a boiling solution of ergosta-7,22-dien-3-one (20 g.) and potassium t-butoxide (from 4·5 g. of potassium) in benzene (200 ml.) and t-butyl alcohol (200 ml.). The mixture was refluxed for a further 30 min. then worked up through ether, and the crude product (6 spots on a thin-layer chromatogram) chromatographed on alumina (1 kg.) with light petroleum–benzene (1 : 1) as eluant. The first fraction (1200 ml. of eluate) yielded, after fractional crystallisation from hexane–ethanol and then from chloroform–methanol, a mixture (750 mg.), which showed 4 spots on a thin-layer chromatogram, and a *bis-steroid* (420 mg.), m. p. 352—355°, $[\alpha]_D$ ±0° (*c* 0·55), $\nu_{max.}$ 1709 cm.$^{-1}$ [Found: C, 86·9, 87·0; H, 11·3, 11·4%; *M* (Rast), 860. $C_{57}H_{88}O$ requires C, 86·7; H, 11·2%; *M*, 789]. The second fraction (2 l. of eluate) gave a mixture (11·3 g.) that showed 6 spots on a thin-layer chromatogram. The third fraction (6·5 l. of eluate) furnished 4α-methylergosta-7,22-dien-3-one (5·9 g.).

Reduction of 4α-Methylergosta-7,22-dien-3-one with Metal Hydrides.—(*a*) A solution of the ketone (4·2 g.) in dioxan (500 ml.) and water (50 ml.) was heated (30 min. on a steam-bath with sodium borohydride (2·5 g.). The product, isolated in the usual manner, showed 2 spots on a thin-layer chromatogram and was chromatographed on silica gel (200 g.). Elution with chloroform (400 ml.) and crystallisation, first from hexane and finally from methanol, afforded matted needles (390 mg.) of *4α-methylergosta-7,22-dien-3α-ol*, m. p. 167—167·5°, $[\alpha]_D$ −37 ± 2° (*c* 0·70), $\nu_{max.}$ 1070 cm.$^{-1}$ (Found: C, 84·2; H, 11·6. $C_{29}H_{48}O$ requires C, 84·4; H, 11·7%). Acetylation furnished the *acetate*, m. p. 186—187° (needles, from chloroform–methanol), $[\alpha]_D$ −46° (*c* 0·80), $\nu_{max.}$ (in CS_2) 1250sh, 1241, 1235, 1190, and 1018 cm.$^{-1}$ (Found: C, 81·6; H, 11·0. $C_{31}H_{50}O_2$ requires C, 81·9; H, 11·1%).

Further elution of the column with chloroform (450 ml.) gave a mixture (2·9 g.) that showed 2 spots on a thin-layer chromatogram. Elution with more chloroform (500 ml.) afforded, after crystallisation from hexane and then methanol, needles (1·2 g.) of *4α-methylergosta-7,22-dien-3β-ol*, m. p. 201—203°, $[\alpha]_D$ −27° (*c* 1·13), $\nu_{max.}$ 1055 cm.$^{-1}$ (Found: C, 84·5; H, 11·4%). Acetylation yielded needles of the *acetate*, m. p. 176—177°, $[\alpha]_D$ +1 ± 2° (*c* 0·88), $\nu_{max.}$ (in CS_2) 1242 and 1036 cm.$^{-1}$ (Found: C, 81·6; H, 10·8%).

Repeated chromatography of the mixed fraction, together with the mother-liquor material from the crystallisations, yielded more 3α-ol (290 mg.) and 3β-ol (1·6 g.).

(*b*) The ketone (300 mg.) in tetrahydrofuran (30 ml.) was refluxed (1·5 hr.) with lithium aluminium hydride (600 mg.), and the mixture worked up as described above to give the 3α-ol (45 mg.) and the 3β-ol (205 mg.).

(*c*) The ketone (300 mg.) in pyridine (40 ml.) was left overnight at room temperature with lithium aluminium hydride (600 mg.). Standard manipulation gave the 3α-ol (40 mg.) and the 3β-ol (175 mg.).

(*d*) The ketone (300 mg.) in tetrahydrofuran (30 ml.) was left (5 days) at room temperature with lithium tri-t-butoxyaluminium hydride (1 g.). Standard manipulation gave the 3α-ol (30 mg.) and the 3β-ol (225 mg.).

Action of Digitonin on the 4α-Methylergosta-7,22-dien-3-ols.—(*a*) The 3β-ol (10 mg.) in 90% ethanol (10 ml.) was mixed with digitonin (25 mg.) in the same solvent (20 ml.), and the solution left overnight. The precipitated digitonide was dissolved in pyridine (0·5 ml.), and the solution diluted with ether (10 ml.). The filtered solution afforded the 3β-ol (6 mg.).

(*b*) Similar treatment of the 3α-ol failed to give a precipitate even after 1 month.

(*c*) The mixed alcohols (1 : 1; 45 mg.), when similarly treated, slowly yielded a digitonide. After 2 days the digitonide was collected and decomposed to give the 3β-ol (8 mg.).

Ethylene Dithioketal of 4α-Methylergosta-7,22-dien-3-one.—The ketone (213 mg.), ethane-1,2-dithiol (0·2 ml.), and boron trifluoride etherate (0·2 ml.) were stirred to a uniform paste (during *ca.* 2 min.) and the mixture then diluted with methanol (5 ml.). The solid was collected and crystallised from chloroform–methanol to yield the *dithioketal* as plates (220 mg.), m. p. 203—204°, $[\alpha]_D$ −4° (*c* 0·90) (Found: S, 13·1. $C_{31}H_{50}S_2$ requires S, 13·2%).

4α-Methylergost-8(14)-en-3β-ol.—4α-Methylergosta-7,22-dien-3β-yl acetate (590 mg.) in acetic acid (350 ml.) was shaken with hydrogen over platinum until absorption ceased (*ca.* 20 min.). The product, which gave a yellow colour in the tetranitromethane test, was *4α-methylergost-8(14)-en-3β-yl acetate* (550 mg.), m. p. 115—115·5° (needles, from methanol), $[\alpha]_D$ +24° (*c* 0·80) (Found: C, 81·7; H, 11·6. $C_{31}H_{52}O_2$ requires C, 81·5; H, 11·5%). Alkaline hydrolysis

of the acetate furnished the *alcohol*, m. p. 159—160° (needles, from methanol), $[\alpha]_D$ +6° (*c* 0·65) (Found: C, 83·8; H, 11·9. $C_{29}H_{50}O$ requires C, 84·0; H, 12·15%).

The 8(14)-enyl acetate (15 mg.) in ether (3 ml.) was left (9 days) at room temperature with osmium tetroxide (25 mg.) and pyridine (2 drops). The mixture was refluxed (1 hr.) and then evaporated to dryness, and the residue treated with lithium aluminium hydride (200 mg.) in refluxing tetrahydrofuran (5 ml.) for 30 min. The crude product, isolated in the usual manner, was left (2 days) at room temperature with lead tetra-acetate (25 mg.) in acetic acid (1 ml.) containing t-butyl alcohol (0·1 ml.). The reaction mixture was diluted with water and extracted with methylene dichloride, and the extract filtered through alumina (3 g.) and then evaporated to dryness. A solution of the residue in carbon disulphide (2 ml.) was used for the infrared spectrum which showed strong bands at 1736 and 1712 cm.$^{-1}$.

4α-*Methylergostan*-3β-*ol*.—(*a*) 4α-Methylergost-8(14)-en-3β-yl acetate (200 mg.) in acetic acid (200 ml.) containing concentrated hydrochloric acid (10 ml.) was shaken (48 hr.) with hydrogen over platinum. The product, isolated in the usual manner, was crystallised first from hexane–ethanol and then from methanol to give needles (155 mg.) of 4α-*methylergostan*-3β-*yl acetate*, m. p. 153—153·5°, $[\alpha]_D$ +28 ± 1° (*c* 0·73), which shows no selective absorption in the ultraviolet above 200 mμ and does not give a colour in the tetranitromethane test (Found: C, 81·2; H, 11·6. $C_{31}H_{54}O_2$ requires C, 81·15; H, 11·9%). Alkaline hydrolysis of the acetate afforded 4α-*methylergostan*-3β-*ol*, m. p. 188—189° (needles, from hexane–ethanol), $[\alpha]_D$ +13° (*c* 0·68) (Found: C, 83·3; H, 12·5. $C_{29}H_{52}O$ requires C, 83·6; H, 12·6%).

(*b*) In a similar experiment 4α-methylergosta-7,22-dien-3β-yl acetate (100 mg.) gave the saturated acetate (85 mg.), m. p. 152—153°, $[\alpha]_D$ +29° (*c* 0·73).

(*c*) Hydrogen chloride was passed into a solution of 4α-methylergost-8(14)-en-3β-yl acetate (50 mg.) in chloroform (20 ml.) for 3 hr. The washed (H_2O) and dried (Na_2SO_4) solution was evaporated to dryness to give a crystalline residue, which was dissolved in ethyl acetate (50 ml.) and shaken (24 hr.) with hydrogen over platinum. The crude product, after chromatography on alumina (5 g.), afforded 4α-methylergostan-3β-yl acetate (25 mg.) and starting material (12 mg.).

4α-*Methylergostan*-3-*one*.—Oxidation of 4α-methylergostan-3β-ol (50 mg.) with chromium trioxide in pyridine furnished the saturated *ketone* (35 mg.), m. p. 146—147° (needles from chloroform–methanol), $[\alpha]_D$ +6 ± 1° (*c* 0·92), $\nu_{max.}$ 1708 cm.$^{-1}$ (Found: C, 83·9; H, 12·3. $C_{29}H_{50}O$ requires C, 84·0; H, 12·15%).

4α-*Methylergosta*-7,22-*diene*.—(*a*) Wolff–Kishner reduction of 4α-methylergosta-7,22-dien-3-one (827 mg.) in digol solution for 4 hr. gave a product, chromatography of which on alumina (80 g.) and elution with light petroleum yielded a wax (700 mg.). Repeated crystallisation of this furnished needles (230 mg.) of 4-α-*methylergosta*-7,22-*diene*, m. p. 130·5—131·5° (from ethyl acetate–ethanol), $[\alpha]_D$ −35 ± 2° (*c* 1·0) (Found: C, 87·4; H, 12·45. $C_{29}H_{48}$ requires C, 87·8; H, 12·2%).

(*b*) The ethylene dithioketal (60 mg.) of 4α-methylergosta-7,22-dien-3-one was refluxed overnight with Raney nickel (*ca.* 1 g.) in benzene (30 ml.). The product, isolated in the usual manner and chromatographed on alumina, was 4α-methylergosta-7,22-diene (25 mg.), m. p. 130—131°, $[\alpha]_D$ −33° (*c* 0·92).

4α-*Methylergostane*.—(*a*) 4α-Methylergosta-7,22-diene (195 mg.) in ethyl acetate (30 ml.) and acetic acid (30 ml.) containing concentrated hydrochloric acid (5 ml.) was shaken (40 hr.) with hydrogen over platinum. Standard isolation procedure furnished 4α-*methylergostane* (100 mg.), m. p. 99—99·5° (needles, from hexane–ethanol), $[\alpha]_D$ +8 ± 1° (*c* 0·85), which is transparent in the ultraviolet above 200 mμ, does not give a colour in the tetranitromethane test, and cannot be detected on a thin-layer chromatogram with the chlorosulphonic acid spray (Found: C, 86·7; H, 13·1. $C_{29}H_{52}$ requires C, 86·9; H, 13·1%).

(*b*) Wolff–Kishner reduction of 4α-methylergostan-3-one (28 mg.) in digol solution for 4 hr. and crystallisation of the crude product from hexane–ethanol gave the *azine* (10 mg.), m. p. 255—255·5°, $[\alpha]_D$ −75° (*c* 0·52), $\nu_{max.}$ 1639 cm.$^{-1}$ (C=N) (Found: N, 3·0. $C_{58}H_{100}N_2$ requires N, 3·4%). The mother-liquors from the crystallisations were combined and the residue chromatographed on alumina (2 g.). Elution with light petroleum (25 ml.) and crystallisation from hexane–ethanol afforded the saturated hydrocarbon (5 mg.), m. p. 96—98°, $[\alpha]_D$ +7° (*c* 0·33).

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