327. *Steroids and Walden Inversion. Part XXX.* The Epimeric Coprostan-3-ylamines and Cholest-4-en-3-ylamines.*

By C. W. Shoppee, D. E. Evans, H. C. Richards, and G. H. R. Summers.

Cholestan-3-one oxime, on reduction with sodium–ethanol, gives cholestan-3β-ylamine, but on hydrogenation with platinum in acetic acid affords cholestan-3α-ylamine, and on reduction with lithium aluminium hydride yields both epimeric bases.

Coprostan-3-one oxime on reduction with sodium–ethanol, on hydrogenation, and on reduction with lithium aluminium hydride, appears to yield only coprostan-3α-ylamine, also obtained by ammonolysis of coprostan-3β-yl toluene-*p*-sulphonate. Coprostan-3β-ylamine was prepared by ammonolysis of coprostan-3α-yl toluene-*p*-sulphonate.

The reduction of cholest-4-en-3-one oxime with sodium–ethanol and lithium aluminium hydride and of cholest-5-en-3-one oxime with lithium aluminium hydride have been examined.

In connexion with other studies, we have recently established the configuration at $C_{(3)}$ of 3β-cholesterylamine,[1] 3α-cholesterylamine,[2] and cholestan-3α-ylamine;[3] the configuration

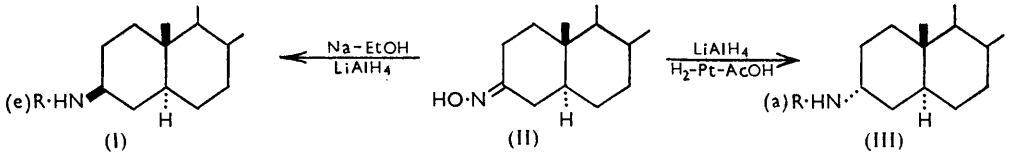
* Part XXIX *J.*, 1956, 1064.

[1] Pierce, Shoppee, and Summers, *J.*, 1955, 690.
[2] Richards, Sly, Shoppee, and Summers, *J.*, 1955, 1054.
[3] Pierce, Richards, Shoppee, Stephenson, and Summers, *J.*, 1955, 694.

of cholestan-3β-ylamine is already known from the work of Haworth, McKenna, and Powell.[4] We now describe the preparation and establish the configuration at $C_{(3)}$ of the epimeric coprostan-3-ylamines and of the acetyl derivatives of the epimeric cholest-4-en-3-ylamines.

The reduction of oximes of unsymmetrical *cyclo*hexanones with sodium and alcohol gives the equatorial amines, whereas catalytic hydrogenation in acid media generally yields the axial amines.[5, 6, 7] We have found [8] that use of lithium aluminium hydride also affords the axial amines with varying amounts of their equatorial isomerides; a similar observation has been made simultaneously by Labler, Czerny, and Sorm,[9] and more recently by Bannard and McKay.[10] Although steroid 3-ketones should give two geometrically isomeric oximes, one isomeride appears to be formed predominantly or exclusively and the oximes used in the following work appeared to be homogeneous individuals.

Cholestan-3-one oxime (II), on reduction with sodium–ethanol,[11] gave exclusively cholestan-3β-ylamine (I; R = H). Although sodium borohydride in methanol at 20° and 65° was ineffective, use of lithium aluminium hydride afforded cholestan-3α-ylamine (III; R = H), accompanied by an approximately equal quantity [9] of cholestan-3β-ylamine (I; R = H); the bases and their acetyl derivatives were separated chromatographically. Catalytic reduction with platinum in dioxan failed, but proceeded smoothly and rapidly in acetic acid to give exclusively cholestan-3α-ylamine (III; R = H), isolated as the acetyl derivative.



(I) (II) (III)

R = H : m. p. 117°,[9] 120°,[11]
m. p. 118—119°, $[\alpha]_D$ +29° †
R = Ac : m. p. 243°, $[\alpha]$ +12°,[3]
m. p. 246°,[4]
m. p. 245°, $[\alpha]_D$ +12° †

R = H : m p. 88°,[9]
m. p. 87—88°, $[\alpha]_D$ +27° †
R = Ac : m. p. 216°, $[\alpha]_D$ +33°,[16]
m. p. 217°, $[\alpha]_D$ +36° †

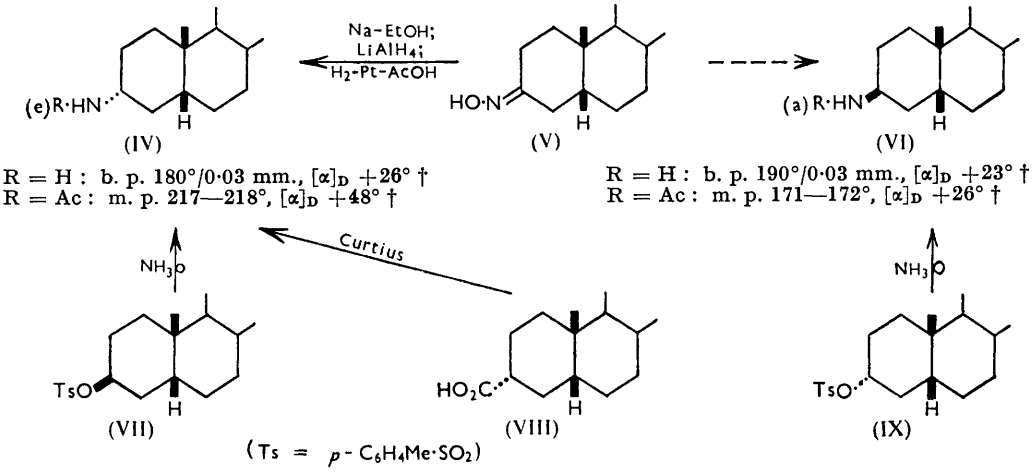
Coprostan-3-one oxime (V) by reduction with sodium in ethanol gave coprostan-3α-ylamine (IV; R = H), identical with the base produced (*a*) by Curtius degradation of coprostane-3α-carboxylic acid [2] (VIII) and (*b*) by ammonolysis of coprostan-3β-yl toluene-*p*-sulphonate (VII). Reduction with lithium aluminium hydride gave, contrary to expectation, only coprostan-3α-ylamine (IV; R = H); subsequent reductions with new specimens of the reagent failed, despite extensive variation of the experimental conditions and careful chromatography, to yield coprostan-3β-ylamine (VI; R = H),[8] which was obtained by ammonolysis of coprostan-3α-yl toluene-*p*-sulphonate (IX). Catalytic hydrogenation of coprostan-3-one oxime (V) with platinum in dioxan failed, but in acetic acid proceeded smoothly, rapidly, and contrary to expectation [cf. (II) ⟶ (III)] to give exclusively coprostan-3α-ylamine (IV; R = H), isolated as the acetyl derivative.

The reduction of coprostan-3-one oxime (V) with lithium aluminium hydride to give exclusively coprostan-3α-ylamine [IV; R = H (3α-NH_2 equatorial)] is surprising because under comparable conditions (*a*) pregnan-3-one oxime (as V) yielded mainly pregnan-3β-ylamine [as VI; R = H (3β-NH_2 axial)] as an oil, b. p. 120—140°/0·02 mm., which crystallised, m. p. 65—78°, and was characterised [3] as the acetyl derivative, m. p. 213°, and by

† Values so marked are from this paper.

[4] Haworth, McKenna, and Powell, *J.*, 1953. 1110.
[5] McNiven and Read, *J.*, 1952, 153.
[6] Barton, *J.*, 1953, 1027.
[7] Cremlyn, Garmaise, and Shoppee, *J.*, 1953, 1847.
[8] Evans, Shoppee, and Summers, *Chem. and Ind.*, 1954, 1535.
[9] Labler, Czerny, and Sorm, *Chem. Listy*, 1954, **48**, 1058.
[10] Bannard and McKay, *Canad. J. Chem.*, 1955, **33**, 1166.
[11] Dodgson and Haworth, *J.*, 1952, 67.

conversion into the dimethyl derivative, m. p. 124°, identical with a specimen prepared by Professor R. D. Haworth, whilst (*b*) reduction of *allo*pregnan-3-one oxime (as II) with lithium aluminium hydride gave *allo*pregnan-3β-ylamine [as I; R = H (3β-NH_2 equatorial)], identical with the base produced by use of sodium–ethanol.[4] The reduction of pregnan-3-one oxime was repeated at that time to provide more material, with the same result; it should, however, be pointed out that the reduction product was not chromatographed and that some of the epimeric pregnan-3α-ylamine [as IV; R = H (3α-NH_2 equatorial)] may have been formed. We feel convinced however that the principal product was undoubtedly pregnan-3β-ylamine (as VI; R = H), and we can only ascribe the

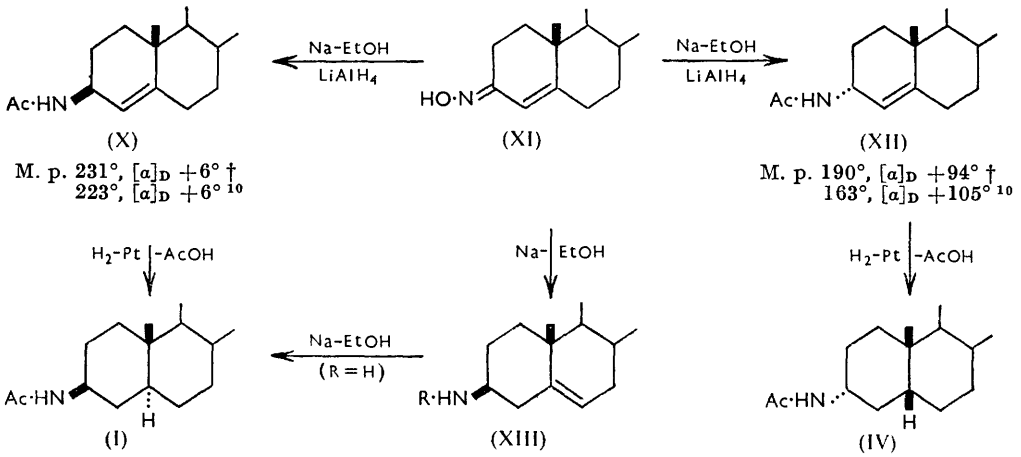


unexpected difference in behaviour between the coprostane and the pregnane series to long-range effects originating in the side-chain and relayed across a relatively rigid saturated molecule.

The reduction of cholest-4-en-3-one oxime (XI) with sodium in ethanol was first examined by Windaus and Adamla,[12] who by acetylation and fractional crystallisation isolated and identified 3β-acetamidocholest-5-ene (14%), m. p. 243°; further fractional crystallisation and, finally, hand-picking yielded two isomerides, " β-acetylcholesterylamine," m. p. 216—217°, and " γ-acetylcholesterylamine," m. p. 190°. We find that reduction of cholest-4-en-3-one oxime (XI) with sodium in ethanol and chromatography of the acetylated product leads to four compounds. One of these, 3β-acetamidocholest-4-ene (X), appears to correspond with the " β-acetylcholesterylamine " of Windaus and Adamla, and by catalytic hydrogenation with platinum in acetic acid affords 3β-acetamidocholestane (I), whilst another, 3α-acetamidocholest-4-ene (XII), appears to be the " γ-acetylcholesterylamine " of Windaus and Adamla, and by catalytic hydrogenation gives 3α-acetamidocoprostane (IV); the two compounds (X) and (XII) can be more readily prepared by reduction of cholest-4-en-3-one oxime with lithium aluminium hydride. The third compound is 3β-acetamidocholestane (I), which may have arisen by reduction of 3β-acetamidocholest-4-ene (X), or by reduction of the fourth compound 3β-acetamidocholest-5-ene [12, 13] (XIII; R = Ac) [as the free base (XIII; R = H) with subsequent acetylation]. The formation of 3β-cholesterylamine (XIII; R = H) in the sodium–ethanol reduction of cholest-4-en-3-one oxime [cf. the sodium–ethanol reduction of cholest-4-en-3-one by Diels and Linn [14]] suggests that in the presence of ethoxide ions an equilibrium is set up between the αβ-unsaturated structure (XIV) and the βγ-unsaturated structure (XVI) in which the former preponderates; addition of a proton to the mesomeric anion (XV)

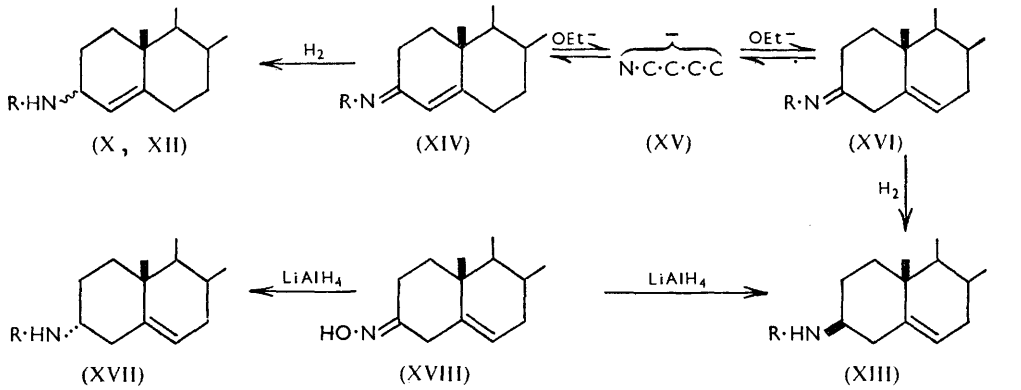
[12] Windaus and Adamla, *Ber.*, 1911, **44**, 3051.
[13] Julian, Magnani, Cole, and Meyer, *J. Amer. Chem. Soc.*, 1948, **70**, 1834.
[14] Diels and Linn, *Ber.*, 1908, **41**, 260; Wagner-Jauregg and Werner, *Z. physiol. Chem.*, 1932, **208**, 72.

under thermodynamic control will lead to production of the epimeric cholest-4-en-3-ylamines (X, XII; R = H), whilst addition to the mesomeric anion (XV) under kinetic control will lead to 3β-cholesterylamine (XIII; R = H).



Reduction of cholest-5-en-3-one oxime [15] (XVIII) with lithium aluminium hydride and chromatographic separation of the resulting bases gave 3β- (XIII; R = H) and 3α-cholesterylamine (XVII; R = H), which were characterised as the acetyl derivatives.

Since this work was completed Bannard and McKay [10] have described the reduction with lithium aluminium hydride of the oximes (XI, XVIII). From cholest-4-en-3-one oxime (XI), they obtained 27% of 3β- (X) and 28% of 3α-acetamidocholest-4-ene (XII) {as a polymorph, m. p. 163°, with substantially the same [α]D (+105°) as our preparation};



from cholest-5-en-3-one oxime (XVIII) by chromatography of the acetylated product they obtained 46% of 3β- (XIII; R = Ac), m. p. 243°, [α]D −45°, and 23% of 3α-acetamidocholest-5-ene (XVII; R = Ac), m. p. 184·5°, [α]D −59°. Bannard and McKay point out that 3α-substituted steroids are generally more dextrorotatory than their 3β-epimerides, and envisage the possibility of reversing the configurations at $C_{(3)}$ of (XIII) and (XVII);

[15] Butenandt and Schmidt-Thomé, *Ber.*, 1936, **69**, 882.
[16] Haworth, Lunts, and McKenna, *J.*, 1955, 986.

this is unnecessary as the correct specific rotation of 3α-acetamidocholest-5-ene is −30°,[3] −31°,[16] and it appears that Bannard and McKay's preparation was contaminated with some difficultly separable and more lævorotatory substance.

Experimental

For general experimental directions, see *J.*, 1956, 1064. $[\alpha]_D$ are in $CHCl_3$.

Cholestan-3α-ylamine and Cholestan-3β-ylamine.—(*a*) Cholestan-3-one oxime (m. p. 192°; 500 mg.) was treated with lithium aluminium hydride (300 mg.) in refluxing ether overnight. The semisolid product (450 mg.) was chromatographed on aluminium oxide (20 g.). Elution with chloroform–methanol (1 : 1) afforded a solid (220 mg.), which by crystallisation from methanol gave plates of cholestan-3α-ylamine, m. p. 87—88°, $[\alpha]_D$ +27° (*c*, 1·1). Elution with methanol gave a solid (200 mg.), which by crystallisation from acetone yielded needles of cholestan-3β-ylamine, m. p. 118—119°, $[\alpha]_D$ +29° (*c*, 0·92).

(*b*) Cholestan-3-one oxime (m. p. 192°; 1·6 g.) was treated with lithium aluminium hydride (1 g.) in refluxing ether for 3 hr. Excess of reagent was destroyed with ethyl acetate at 0°; the precipitated aluminium oxide was filtered off and continuously extracted with ether. After evaporation of the total ethereal extract, the basic products were isolated *via* their hydrochlorides. Acetylation with acetic anhydride in ether at 15° gave a white solid (1·5 g.), which was chromatographed on aluminium oxide (50 g.). Elution with benzene (4 × 100 c.c.) gave a solid (520 mg.), which on recrystallisation from acetone furnished 3α-acetamidocholestane, m. p. 217—218°, $[\alpha]_D$ +36° (*c*, 0·92). Elution with ether–benzene (1 : 9) gave a solid (900 mg.), m. p. 234—245°, which was rechromatographed on aluminium oxide (30 g.), and by elution with benzene (3 × 100 c.c.) also yielded 3α-acetamidocholestane (200 mg.). Further elution with ether–benzene (1 : 9) afforded a solid (650 mg.), which by recrystallisation from acetone gave 3β-acetamidocholestane, m. p. 245—246°, $[\alpha]_D$ +12° (*c*, 1·0).

Cholestan-3α-ylamine.—3α-Acetamidocholestane (200 mg.) was heated under reflux with ethanol (200 c.c.) and concentrated hydrochloric acid (140 c.c.) for 24 hr. The oily product, isolated in the usual way, was chromatographed on aluminium oxide (6 g.); elution with methanol gave cholestan-3α-ylamine as an oil. This was sublimed at 170°/0·03 mm. to afford an oil, which slowly solidified, and, recrystallised from methanol, had m. p. 87—88°, $[\alpha]_D$ +27° (*c*, 1·1).

Cholestan-3β-ylamine.—3β-Acetamidocholestane (200 mg.) was heated under reflux with ethanol (200 c.c.) and concentrated hydrochloric acid (140 c.c.) for 24 hr. The solid product was recrystallised repeatedly from ethanol, to give cholestan-3β-ylamine, m. p. 118°.

Catalytic Reduction of Cholestan-3-one Oxime.—(*a*) Cholestan-3-one oxime (760 mg.) in dioxan (20 c.c.) was shaken under hydrogen in the presence of platinum oxide (140 mg.) for 24 hr. but no reduction of the oxime occurred.

(*b*) Cholestan-3-one oxime (510 mg.) in glacial acetic acid (20 c.c.) was shaken in hydrogen with platinum oxide (100 mg.); the theoretical uptake of hydrogen was attained in 1 hr. The product was acetylated with acetic anhydride in ether at 15°, to yield a solid (500 mg.) which was chromatographed on aluminium oxide (15 g.). Elution with benzene (1 × 50 c.c.) yielded a solid (150 mg.), which by recrystallisation from acetone afforded 3α-acetamidocholestane, m. p. 216—217°. Further elution with benzene gave a solid (330 mg.), m. p. 208°, which was rechromatographed on aluminium oxide (10 g.); elution with benzene again gave 3α-acetamidocholestane (310 mg.), whilst elution with ether–benzene (1 : 9) gave 3β-acetamidocholestane, m. p. 246° (10 mg.), after recrystallisation from ethyl acetate.

Coprostan-3-one Oxime.—Coprostan-3-one was oximated with hydroxylamine acetate in refluxing methanol, and the product (5 g.) chromatographed on aluminium oxide (150 g.). Elution with benzene–pentane (1 : 9) gave coprostan-3-one (120 mg.), whilst elution with acetone afforded the oxime as an oil (4·6 g.). On pouring an ethanolic solution of the oxime into water, a white amorphous solid was obtained, which after intense drying gave coprostan-3-one oxime,[17] m. p. 68°, $[\alpha]_D$ +33° (*c*, 0·92) [Found (after drying at 50°/0·03 mm. for 3 hr.): C, 80·6; H, 11·6. Calc. for $C_{27}H_{47}ON$: C, 80·7; H, 11·8%].

Coprostan-3α-ylamine.—(*a*) Coprostan-3-one oxime (1 g.) in refluxing pentyl alcohol (200 c.c.) was treated with sodium (16 g.) during 3 hr. The solution was worked up in the usual manner and basic material isolated as the pentane-insoluble hydrochloride, which afforded by treatment with ammonia an oily base (900 mg.). The oil was chromatographed on aluminium oxide (10 g.); elution with methanol (10 × 100 c.c.) afforded a yellow oil (800 mg.), which was

[17] Dorée and Gardener, *J.*, 1908, 1625.

distilled at 180°/0·03 mm., to yield *coprostan-3α-ylamine* as a colourless oil, $[\alpha]_D$ +26° (*c*, 1·2) [Found : C, 83·6; H, 12·7. $C_{27}H_{49}N$ requires C, 83·7; H, 12·65%]. Acetylation with acetic anhydride in ether at 15° gave a solid product, which by recrystallisation from acetone furnished 3α-*acetamidocoprostane* m. p. 218—219°, $[\alpha]_D$ +48° (*c*, 0·92) [Found (after drying at 100°/0·03 mm. for 3 hr.) : C, 80·9; H, 11·9. $C_{29}H_{51}ON$ requires C, 81·1; H, 11·9%].

(*b*) Coprostan-3-one oxime (850 mg.) was treated with lithium aluminium hydride (480 mg.) in refluxing ether for 5 hr. The mixture was worked up in the usual manner to give an oily base (700 mg.) which on acetylation with acetic anhydride in ether at 15° gave a solid which was chromatographed on aluminium oxide (20 g.). Elution with ether–benzene (1 : 9) gave a solid (680 mg.) which by crystallisation from acetone yielded 3α-acetamidocoprostane, m. p. 217—218°.

(*c*) Coprostan-3-one oxime (1 g.) in acetic acid (20 c.c.) was hydrogenated with platinum oxide (325 mg.); the theoretical uptake of hydrogen was attained in 1·5 hr. The oily product was acetylated in ether at 15° to yield a solid (920 mg.), which was chromatographed on aluminium oxide (30 g.). Elution with ether–benzene (1 : 9) afforded only 3α-acetamidocoprostane, m. p. and mixed m. p. 218°.

(*d*) Coprostan-3β-yl toluene-*p*-sulphonate (600 mg.) was heated at 100° in an autoclave with liquid ammonia; the mixture was worked up in the usual manner and acetylated with acetic anhydride in ether at 15° to afford a solid (510 mg.). This was chromatographed on aluminium oxide (15 g.); elution with ether–benzene (1 : 9) gave 3α-acetamidocoprostane, m. p. 217—218°, $[\alpha]_D$ +48° (*c*, 1·0).

Coprostan-3β-ylamine.—Coprostan-3α-yl toluene-*p*-sulphonate (3·9 g.) was heated at 100° in an autoclave with liquid ammonia, the reaction mixture was worked up in the usual manner and the product chromatographed on aluminium oxide (60 g.). Successive elution with benzene, ether, and methanol gave oily fractions, which by distillation at 190°/0·03 mm. gave coprostan-3β-ylamine as an oil, $[\alpha]_D$ +23° (*c*, 0·73) [Found : C, 83·1; H, 12·7. $C_{27}H_{49}N$ requires C, 83·7; H, 12·65%]. Acetylation with acetic anhydride at 100° gave a solid, which by crystallisation from acetone yielded 3β-*acetamidocoprostane*, m. p. 172°, $[\alpha]_D$ +26° (*c*, 1·13) [Found (after drying at 100°/0·03 mm.) : C, 81·1; H, 12·1. $C_{29}H_{51}ON$ requires C, 81·1; H, 11·9%].

Sodium–Ethanol Reduction of Cholest-4-en-3-one Oxime.—Cholest-4-en-3-one oxime (5 g.), m. p. 153°, in boiling ethanol (200 c.c.) was treated with sodium (20 g.). The product, worked up in the usual way, was an oil, which on acetylation in ether at 15° yielded a solid. This was chromatographed on aluminium oxide (100 g.); elution with benzene–pentane (1 : 1) (4 × 200 c.c.) gave an oil which crystallised from ethyl acetate in needles, m. p. 186—190°, $[\alpha]_D$ +97° (*c*, 1·1). Elution with benzene (3 × 200 c.c.) gave a solid, m. p. 205—222°, and further elution with benzene (8 × 200 c.c.) yielded 3β-acetamidocholest-5-ene, m. p. and mixed m. p. 239—243°, $[\alpha]_D$ −40° (*c*, 0·8). Finally, elution with chloroform–ether gave a small quantity of oil. The fraction, m. p. 205—222° was rechromatographed on aluminium oxide (75 g.); elution with benzene (3 × 100 c.c.) gave oils, but further use of benzene (2 × 100 c.c.) gave a solid, m. p. 182—189°, $[\alpha]_D$ +90°, which crystallised from ethyl acetate in needles, m. p. 189—190°, $[\alpha]_D$ +97° (*c*, 0·73); whilst still further use of benzene (3 × 100 c.c.) gave a solid, m. p. 228—230°, $[\alpha]_D$ +7° (*c*, 0·7), and final elution with benzene gave mixtures, m. p. 216—235°, and a solid, $[\alpha]_D$ +10° (*c*, 0·85), m. p. 240—244° undepressed on admixture with 3β-acetamidocholestane. The acetylated bases, m. p. 189—190°, $[\alpha]_D$ +97°, and m. p. 228—230°, $[\alpha]_D$ +7°, were identical with 3α- and 3β-acetamidocholest-4-ene respectively described below.

3α-*Acetamidocholest-4-ene and* 3β-*Acetamidocholest-4-ene.*—Cholest-4-en-3-one oxime (1·8 g.), m. p. 153°, in ether (200 c.c.) was refluxed with lithium aluminium hydride (1·6 g.) for 4 hr. Working up the product in the usual way, followed by acetylation in ether at 15°, gave a yellow solid (1·8 g.), which was chromatographed on aluminium oxide (60 g.). Elution with benzene–pentane (1 : 1) gave a small amount of oil, which by crystallisation from ethyl acetate gave 3α-*acetamidocholest-4-ene*, m. p. 190°, $[\alpha]_D$ +94° (*c*, 1·23) [Found (after drying at 25°/0·03 mm. for 16 hr.) : C, 81·7; H, 11·4. $C_{29}H_{49}ON$ requires C, 81·5; H, 11·5%]. Further elution with benzene–pentane (1 : 1) and ether–benzene gave a solid (1 g.), which by crystallisation from ethyl acetate gave 3β-*acetamidocholest-4-ene*, m. p. 231°, $[\alpha]_D$ +6° (*c*, 0·87) [Found (after drying at 25°/0·03 mm. for 16 hr.) : C, 81·3; H, 11·3%].

3α-*Acetamidocoprostane.*—3α-Acetamidocholest-4-ene (20 mg.) in glacial acetic acid (10 c.c.) was hydrogenated with platinum oxide (10 mg.) for 2 hr. Working up in the usual way gave a solid, which crystallised from acetone in plates, m. p. 180—215°, and after sublimation (210°/0·01 mm.) and recrystallisation from ethyl acetate gave 3α-acetamidocoprostane, m. p. 215°, mixed m. p. 212—215°, $[\alpha]_D$ +47° (*c*, 0·8).

3β-*Acetamidocholestane.*—3β-Acetamidocholest-4-ene (350 mg.) in glacial acetic acid (20 c.c.) and ether (100 c.c.) was hydrogenated with platinum oxide (100 mg.) for 4 hr. Working up in the usual way gave a solid (350 mg.), which was chromatographed on aluminium oxide (10 g.). Elution with benzene gave a solid, which crystallised from acetone in plates, $[\alpha]_D$ +12° (*c*, 1·12), m. p 241—243°, undepressed on admixture with 3β-acetamidocholestane.

[With J. H. PIERCE] *Cholest-5-en-3β-ylamine and Cholest-5-en-3α-ylamine.*—Cholest-5-en-3-one oxime (9 g.), m. p. 188°, in boiling ether (200 c.c.) was reduced with lithium aluminium hydride (5 g.). The mixture of bases was isolated as an oil (7·9 g.), and a portion (6 g.) was chromatographed on aluminium oxide (180 g.). Elution with benzene–pentane and with benzene gave uncrystallisable oils, whilst ether–benzene (1 : 9) (20 × 100 c.c.) gave an oil, which crystallised (m. p. 86—88°) and after distillation at 130°/0·02 mm. yielded cholest-5-en-3α-ylamine as needles (from cooled pentane), m. p. 100°, $[\alpha]_D$ −40° (*c*, 0·89). Acetylation in ether at 15° yielded 3α-acetamidocholest-5-ene, which crystallised from acetone as needles, m. p. 186—189°, $[\alpha]_D$ −30° (*c*, 1·0). Elution with ether–benzene (1 : 4) gave oils, whilst ether (18 × 100 c.c.) gave an oil, which on crystallisation from acetone yielded needles, m. p. 138—140° undepressed by the *iso*propylidene derivative of cholest-5-en-3β-ylamine. Acetylation gave 3β-acetamidocholest-5-ene, m. p. and mixed m. p. 243°.

[With J. H. PIERCE] allo*Pregnan*-3β-*ylamine.*—*allo*Pregnan-3-one oxime (m. p. 196°; 0·5 g.) in boiling ethanol (20 c.c.) was reduced with sodium (4 g.). Working up in the usual way gave an oil, which by distillation at 130—140°/0·01 mm. gave allo*pregnan*-3β-*ylamine*, m. p. 119°, $[\alpha]_D$ +6·6° (*c*, 1·2) (Found : C, 82·9; H, 12·1. $C_{21}H_{37}N$ requires C, 83·3; H, 12·0%). Acetylation with acetic anhydride in ether at 15° gave a solid, which after sublimation at 220—240°/0·01 mm. and crystallisation from acetone gave 3β-*acetamido*allo*pregnane*, m. p. 266—268°, $[\alpha]_D$ 0° (*c*, 0·5) [Found (after drying at 100°/0·01 mm. for 4 hr.) : C, 79·8; H, 11·4. $C_{23}H_{39}ON$ requires C, 79·9; H, 11·4%].

*allo*Pregnan-3-one oxime (250 mg.) was treated with lithium aluminium hydride (150 mg.) in refluxing ether for 5 hr. Working up in the usual way gave an oil, which by acetylation with acetic anhydride in ether at 15° and crystallisation from ethyl acetate gave needles, m. p. 265°, undepressed by the above specimen of 3β-acetamido*allo*pregnane.

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