873. *Steroids and Walden Inversion. Part XXXVIII.* The Deamination of Epimeric Cholestan-2-, -4-, and -7-ylamines.*

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Deamination in aqueous acetic acid of the equatorial cholestan-2α-, -4α-, and -7β-ylamines gives cholestan-2α-, -4α-, and -7β-ol respectively in high yield unaccompanied by the epimeric alcohols. The axial cholestan-2β-, -4β-, and -7α-ylamines yield cholestan-2β-, -4β-, and -7α-ol respectively accompanied by much cholest-2-, -4-, and -7-ene, respectively.

Shoppee, Evans, and Summers [1] found that deamination in aqueous acetic acid of epimeric 3- and 6-amino-steroids follows a strict stereochemical pattern; the equatorial amines react with retention of configuration to afford the appropriate equatorial alcohols in quantitative yield, whilst the axial amines react, also with retention of configuration, uniquely to furnish the appropriate axial alcohols accompanied by much elimination, the olefins produced conforming to the Saytzeff rule. A preliminary examination of the deamination of the epimeric cholestan-7-ylamines was reported; this work has now been completed and the investigation extended to include the epimeric cholestan-2- and -4-ylamines.

The epimeric bases were prepared by the standard methods; the oximes of cholestan-2-,[2] -4-,[3] and -7-one [4] on reduction with sodium–ethanol gave cholestan-2α-, -4α-, and -7β-ylamine (NH_2 : equatorial), and on catalytic reduction with platinum–acetic acid gave the epimeric cholestan-2β-, -4β-, and -7α-ylamines (NH_2 : axial).

Eckhardt [5] had previously prepared the *N*-acetyl derivatives of 3β-hydroxycholest-5-en-7α- and -7β-ylamine, obtained by sodium–ethanol reduction of 3β-acetoxycholest-5-en-7-one oxime. In a repetition of this work Barnett, Ryman, and Smith [6] succeeded in separating the free bases by fractional crystallisation; they also describe 3β-hydroxycholestan-7α-ylamine, m. p. 87—89°, $[\alpha]_D$ −143°, but it is evident from the rotation that the hydrogenation of 3β-hydroxycholest-5-en-7α-ylamine was incomplete.

The configurations assigned here are based on analogy, unsupported by independent proof as in the previous work,[1] but we regard them as tolerably secure.

The molecular-rotation contributions of the 2-, 4-, and 7-hydroxyl and -acetoxyl groups are set out in Table 1. It will be seen that the values form a consistent series with the β-epimeride always the more dextrorotatory.

In Table 2 are given the molecular-rotation contributions of the 2-, 4-, and 7-amino- and -acetamido-groups. It is seen that the values (except for 4β-acetamidocholestane) again form a consistent series, parallel to that shown in Table 1, and with the β-epimeride always the more dextrorotatory. These comparisons strongly support, if they do not prove, our assignments of configuration to the various pairs of epimeric bases.

The results of the deaminations are set out in Table 3, and reproduce the stereochemical pattern found previously [1] and described above.

The epimeric cholestan-7-ylamines possess purely equatorial and purely axial character respectively, because ring B has a rigid chair conformation on account of double locking by rings A and C. The formation of a single cholestan-7-ol with retention of configuration from each base indicates that partial axial character, arising from chair–boat interconversions, is not a factor in the stereochemical course of deamination of 2-, 3-, and 4-amino-steroids.

* Part XXXVII, *J.*, 1957, 3100.

[1] Shoppee, Evans, and Summers, *J.*, 1957, 97.
[2] Ruzicka, Plattner, and Furrer, *Helv. Chim. Acta*, 1944, **27**, 524.
[3] Barton and Rosenfelder, *J.*, 1951, 1048.
[4] Cremlyn and Shoppee, *J.*, 1954, 3515.
[5] Eckhardt, *Ber.*, 1938, **71**, 461.
[6] Barnett, Ryman, and Smith, *J.*, 1946, 528.

TABLE 1.

	$[M]_D$ ROH	$[M]_D$ parent compound	ΔM_D	$[M]_D$ ROAc	$[M]_D$ parent compound	ΔM_D
Cholestan-2α-ol	+101°	+ 91°	+ 10°	+ 61°	+ 91°	− 30°
Cholestan-2β-ol	+132	+ 91	+ 41	+114	+ 91	+ 23
Cholestan-4α-ol	+ 19	+ 91	− 72	+ 7	+ 91	− 84
Cholestan-4β-ol	+116	+ 91	+ 25	+ 84	+ 91	− 7
Cholestan-7α-ol	+ 43	+ 91	− 48	− 52	+ 91	−143
Cholestan-7β-ol	+202	+ 91	+111	+262	+ 91	+171
Cholestane-3β : 7α-diol	+ 32	+ 93	− 61	− 79 *	+ 60	−139
Cholestane-3β : 7β-diol	+214	+ 93	+121	+268 *	+ 60	+208
Cholest-5-ene-3β : 7α-diol	−382	−151	−231	−850 *	−205	−645
Cholest-5-ene-3β : 7β-diol	+ 29	−151	+180	+262 *	−205	+467

* 3 : 7-Diacetate.

TABLE 2.

	$[M]_D$ NH_2	$[M]_D$ parent compound	ΔM_D	$[M]_D$ NHAc	$[M]_D$ parent compound	ΔM_D
Cholestan-2α-ylamine	+ 77°	+ 91°	− 14°	− 61°	+ 91°	−152°
Cholestan-2β-ylamine	+110	+ 91	+ 19	+118	+ 91	+ 27
Cholestan-4α-ylamine	+ 41	+ 91	− 50	+155	+ 91	+ 64
Cholestan-4β-ylamine	+233	+ 91	+142	+142	+ 91	+ 51
Cholestan-7α-ylamine	− 77	+ 91	−169	+ 17	+ 91	+ 81
Cholestan-7β-ylamine	+209	+ 91	+118	+262	+ 91	+171
3β-Hydroxycholestan-7α-ylamine	− 97	+ 93	−190	− 40	+ 93	−133
3β-Hydroxycholestan-7β-ylamine	+411	+ 93	+318	+280	+ 93	+187
3β-Hydroxycholest-5-en-7α-ylamine	−1395	−151	−1244	−797	−151	−646
3β-Hydroxycholest-5-en-7β-ylamine	+822	−151	+973	+359	−151	+510

TABLE 3.

Amine	Conformn. of NH_2	Product of substitution	Product of elimination
Cholestan-2α-yl	e	Cholestan-2α-ol (96%) Cholestan-2β-ol (0%)	—
Cholestan-2β-yl	a	Cholestan-2β-ol (21%) Cholestan-2α-ol (0%)	Cholest-1- and -2-ene (74·5%)
Cholestan-4α-yl	e	Cholestan-4α-ol (82%) Cholestan-4β-ol (0%)	—
Cholestan-4β-yl	a	Cholestan-4β-ol (0%) Cholestan-4α-ol (0%)	Cholest-4-ene (92%)
Cholestan-7α-yl	a	Cholestan-7α-ol (36·5%) Cholestan-7β-ol (0%)	Cholest-7-ene (61%)
Cholestan-7β-yl	e	Cholestan-7β-ol (95%) Cholestan-7α-ol (0%)	—
3β-Hydroxycholest-5-en-7α-yl	a	Cholest-5-ene-3β : 7α-diol (22%) Cholest-5-ene-3β : 7β-diol (0%)	Cholesta-5 : 7-dien-3β-ol (70%)
3β-Hydroxycholest-5-en-7β-yl	e	Cholest-5-ene-3β : 7β-diol (84%) Cholest-5-ene-3β : 7α-diol (0%)	—
3β-Hydroxycholestan-7α-yl	a	Cholestane-3β : 7α-diol (23%) Cholestane-3β : 7β-diol (0%)	Cholest-7-en-3β-ol (59%)
3β-Hydroxycholestan-7β-yl	e	Cholestane-3β : 7β-diol (75%) Cholestane-3β : 7α-diol (0%)	—
Cholest-4-en-7β-yl	e	Cholest-4-en-7β-ol (86·5%) Cholest-4-en-7α-ol (0%)	—

Product alcohols isolated as acetates, but yields are for pure alcohols calculated from the yields of acetates.

In the case of axial cholestanylamines, there appears to be a connexion between the degree of steric hindrance to the approach of the entity which furnishes the hydroxyl group eventually found in the appropriate axial cholestanol and product composition.

The order of decreasing steric hindrance at the relevant nuclear carbon atoms, estimated by consideration of the number and character of the 1 : 3-interactions, is: 4β = 6β > 2β > [1α] = >7α > 3α. This sequence is also that of decreasing production of olefin (92, 99, 75, 61, 54%) and of increasing production of axial alcohol (0, 0, 21, 37, 45%).

It should be noted that the olefin produced by deamination of cholestan-4β-ylamine is cholest-4-ene unaccompanied by cholest-3-ene, and that cholestan-7α-ylamine gives cholest-7-ene, unaccompanied by cholest-6-ene; these eliminations thus conform to the Saytzeff rule and not to the Hofmann rule.

Experimental

For general experimental directions, see Shoppee, Evans, and Summers.[1] $[\alpha]_D$ are in $CHCl_3$.

Deamination of Steroid Amines.—In the following eleven experiments the steroid amine was dissolved in either glacial acetic acid or 50% acetic acid and where necessary dioxan was added to cause complete dissolution. Sodium nitrite (approximately two to three times the weight of amine) in either water or 50% acetic acid was added, and the mixture left overnight at 20°. After neutralisation with 4N-sodium hydroxide the product was isolated by extraction with ether and then hydrolysed for 0·5 hr. with 5% methanolic potassium hydroxide or acetylated with acetic anhydride at 100°. Chromatographic separations were carried out on activated aluminium oxide (Spence, Type " H," 30 × wt. of product).

(1) Cholestan-2α-ylamine (292 mg.) gave a product which by chromatography yielded a solid (280 mg.; eluted with ether) which by recrystallisation from acetone gave cholestan-2α-ol, m. p. 178—80°, $[\alpha]_D$ +25·7° (*c* 0·88). Acetylation with boiling acetic anhydride gave an oil which by crystallisation from acetone–methanol gave 2α-*acetoxycholestane*, m. p. 60—62°, $[\alpha]_D$ +14° (*c* 1·4) [Found (after drying at 20°/0·03 mm. for 16 hr.): C, 81·0; H, 11·9. $C_{29}H_{50}O_2$ requires C, 80·9; H, 11·7%].

(2) Cholestan-2β-ylamine as its *iso*propylidene derivative (210 mg.) gave a product which by chromatography yielded an oil (135 mg.; eluted with pentane) which by recrystallisation from acetone gave a mixture of cholest-1- and -2-ene, m. p. 68—71°, $[\alpha]_D$ +47° (*c* 0·98). Elution with ether gave a solid (41 mg.) which by recrystallisation from acetone–pentane gave cholestan-2β-ol, m. p. 155°, $[\alpha]_D$ +33° (*c* 1·0).

(3) Cholestan-4α-ylamine (17 mg.) gave a solid (14 mg.; eluted with benzene) which by crystallisation from methanol yielded cholestan-4α-ol, m. p. 189—190°.

(4) Cholestan-4β-ylamine (80 mg.) gave an oil (71 mg.; eluted with pentane) which by crystallisation from acetone furnished cholest-4-ene, m. p. 79—80°, $[\alpha]_D$ +73° (*c* 1·2).

(5) Cholestan-7α-ylamine (300 mg.) gave an oil (174 mg.; eluted with pentane) which by recrystallisation from acetone yielded cholest-7-ene, m. p. 75—78°, $[\alpha]_D$ +10° (*c* 1·4). Elution with benzene–pentane (1 : 1) and benzene furnished an oil (110 mg.) which by crystallisation from methanol gave cholestan-7α-ol, m. p. 94—96°.

(6) Cholestan-7β-ylamine (200 mg.) gave a solid (180 mg.; eluted with benzene) which by crystallisation from methanol gave cholestan-7β-ol, m. p. 112—113°.

(7) 3β-Hydroxycholest-5-en-7α-ylamine (100 mg.) gave a solid (75 mg.; eluted with 1 : 4 benzene–pentane) which by crystallisation from acetone furnished 7-dehydrocholesteryl acetate, m. p. 127—129°, $[\alpha]$ −83° (*c* 2·2). Elution with benzene afforded cholest-5-ene-3β : 7α-diol diacetate, m. p. 123° (25 mg.), after crystallisation from aqueous acetone.

(8) 3β-Hydroxycholest-5-en-7β-ylamine (210 mg.) gave an oil (213 mg.; eluted with benzene) which by crystallisation from ether–methanol yielded cholest-5-ene-3β : 7β-diol diacetate, m. p. 107—109°, $[\alpha]_D$ +53° (*c* 1·01).

(9) 3β-Hydroxycholestan-7α-ylamine (150 mg.) gave a solid (95 mg.; eluted by 2 : 3 benzene–pentane) which by crystallisation from acetone gave cholest-7-en-3β-yl acetate, m. p. 116—118°, $[\alpha]_D$ +0° (*c* 1·2), probably contaminated with a trace of cholest-6-en-3β-yl acetate, m. p. 112—113°, $[\alpha]_D$ −89°. Successive elution with benzene–pentane (1 : 1) and benzene yielded a solid (43 mg.) which by crystallisation from methanol gave cholestane-3β : 7α-diol diacetate, m. p. 136—138°.

(10) 3β-Hydroxycholestan-7β-ylamine (200 mg.) gave a solid (182 mg.; eluted by 1 : 1 benzene–pentane) which by crystallisation from methanol gave cholestane-3β : 7β-diol diacetate, m. p. 84—86°, $[\alpha]_D$ +54° (*c* 0·8).

(11) Cholest-4-en-7β-ylamine (400 mg.) gave an oil (350 mg.; eluted by pentane) which by crystallisation from acetone gave cholest-4-en-7β-yl acetate, m. p. 95—98° $[\alpha]_D$ +72° (*c* 1·1). Elution with benzene gave 7β-acetamidocholest-4-ene, m. p. 196—198° (41 mg.).

Cholestan-2α-ylamine.—Cholestan-2-one oxime {m. p. 200—202°, $[\alpha]_D$ +7° (*c* 1·0); 900 mg.} in refluxing propan-2-ol (50 c.c.) was treated with sodium until a saturated solution was formed. The solution was worked up in the usual manner, to give an oil (840 mg.) which was chromatographed on aluminium oxide (30 g.). Successive elution with ether–benzene (1 : 1), ether, ether–methanol (9 : 1), and methanol gave oils (725 mg.) which by crystallisation from pentane yielded *cholestan-2α-ylamine* as rods, m. p. 111—113°, $[\alpha]_D$ +20° (*c* 0·97) [Found (after drying at 20°/0·03 mm. for 6 hr.): C, 83·4; H, 12·5. $C_{27}H_{49}N$ requires C, 83·7; H, 12·65%]. Acetylation with acetic anhydride in ether at 15° gave a solid which by recrystallisation from ethyl acetate afforded 2α-*acetamidocholestane* as needles, m. p. 215—216°, $[\alpha]_D$ −14° (*c* 1·0) [Found (after drying at 50°/0·03 mm. for 3 hr.): C, 81·2; H, 11·8. $C_{29}H_{51}ON$ requires C, 81·05; H, 11·95%].

Cholestan-2β-ylamine.—Cholestan-2-one oxime (906 mg.) in glacial acetic acid (30 c.c.) was shaken in hydrogen with platinum oxide (281 mg.); the theoretical uptake of hydrogen was attained in 3 hr. The product after basification with ammonia was chromatographed on aluminium oxide (30 g.). Successive elution with ether–benzene (1 : 1), ether, ether–methanol (9 : 1), and methanol gave oils (789 mg.) which solidified, to give cholestan-2β-ylamine, m. p. 70—76°, $[\alpha]_D$ +28·4° (*c* 1·2). Crystallisation from acetone gave 2β-iso*propylideneamino*-*cholestane* as rods, m. p. 115—117°, $[\alpha]_D$ +4° (*c* 1·1) [Found (after drying at 20°/0·03 mm. for 16 hr.): C, 83·9; H, 12·5. $C_{30}H_{53}N$ requires C, 84·2; H, 12·5%]. The infrared absorption curve in CCl_4 showed a strong band at 1660 cm.$^{-1}$ attributable to a C=N stretching vibration (cf. Haworth, Lunts, and McKenna [7]). Acetylation with acetic anhydride in ether gave 2β-*acetamidocholestane*, double m. p. 117—118° and 148—150° (from methanol), $[\alpha]_D$ +27·5° (*c* 1·0) [Found (after drying at 20°/0·03 mm. for 16 hr.): C, 80·8; H, 11·5. $C_{29}H_{51}ON$ requires C, 81·05; H, 11·95%].

Cholestan-4α-ylamine.—Cholestan-4-one oxime {m. p. 221—223°, $[\alpha]_D$ +124° (*c* 1·5); Windaus [8] recorded m. p. 205°} (500 mg.) in refluxing butan-1-ol (50 c.c.) was treated with sodium until a saturated solution was formed. The product was a solid (453 mg.) which was chromatographed on aluminium oxide (12 g.). Successive elution with ether–benzene (1 : 1) and ether gave a solid (361 mg.) which by crystallisation from ethyl acetate afforded *cholestan-4α-ylamine*, m. p. 96—98°, $[\alpha]_D$ +10·5° (*c* 0·95) [Found (after drying at 20°/0·03 mm. for 16 hr.): C, 83·4; H, 12·3. $C_{27}H_{49}N$ requires C, 83·7; H, 12·65%]. With acetic anhydride in ether it gave 4α-*acetamidocholestane*, m. p. 228—230° (from ethyl acetate), $[\alpha]_D$ +36° (*c* 0·9) [Found (after drying at 100°/0·03 mm. for 5 hr.): C, 81·0; H, 12·0. $C_{29}H_{51}ON$ requires C, 81·05; H, 11·95%].

Cholestan-4β-ylamine.—Cholestan-4-one oxime (180 mg.) in acetic acid (50 c.c.) was shaken in hydrogen with platinum oxide (50 mg.). Uptake of hydrogen was complete in 10 min. Isolation of the product in the usual manner gave an oil which was chromatographed on aluminium oxide (5 g.). Elution with ether and methylene dichloride gave an oily solid (140 mg.) which by distillation at 220°/0·01 mm. furnished cholestan-4β-ylamine, $[\alpha]_D$ +60° (*c* 1·0). Acetylation with acetic anhydride in ether at 15° gave a solid which was chromatographed on aluminium oxide. Elution with benzene gave a solid which by crystallisation from acetone afforded 4β-*acetamidocholestane*, m. p. 190—193°, $[\alpha]_D$ +33° (*c* 1·0) [Found (after drying at 100°/0·03 mm. for 5 hr.): C, 81·0; H, 11·9%].

Cholestan-7β-ylamine.—Cholestan-7-one oxime (m. p. 168—172°; 7·1 g.) in refluxing butan-1-ol (500 c.c.) was treated with sodium (50 g.) during 3 hr. The solution was worked up in the usual manner and basic material isolated as the ether-insoluble hydrochloride, which on treatment with 2N-potassium hydroxide afforded cholestan-7β-ylamine as an oil (2·88 g.), $[\alpha]_D$ +40° (*c* 3·3). Acetylation with acetic anhydride in pyridine gave a solid which on crystallisation from ether–acetone yielded 7β-*acetamidocholestane* as needles, m. p. 148—150°, $[\alpha]_D$ +61° (*c* 1·27) [Found (after sublimation at 180°/0·01 mm.): C, 80·8; H, 11·9; N, 3·4%]. Benzoylation with benzoyl chloride–pyridine at 20° for 16 hr. gave an oil which after chromatography on aluminium oxide gave a solid which on crystallisation from acetone yielded 7β-*benzamido*-*cholestane* as needles, m. p. 174—177°, $[\alpha]_D$ +81° (*c* 0·6) [Found (after drying at 20°/0·01 mm.

[7] Haworth, Lunts, and McKenna, *J.*, 1955, 986.
[8] Windaus, *Ber.*, 1920, **53**, 488.

for 18 hr.): C, 82·9; H, 10·4. $C_{34}H_{53}ON$ requires C, 83·0; H, 10·8%]. The *hydrochloride* prepared in the usual way had m. p. 252—234° [Found (after drying at 110°/0·01 mm. for 4 hr.) C, 76·4; H, 11·9; N, 3·2. $C_{27}H_{50}NCl$ requires C, 76·4; H, 11·9; N, 3·3%].

Cholestan-7α-ylamine and Cholestan-7β-ylamine.—(*a*) Cholestan-7-one oxime (3·3 g.) in ethanol (100 c.c.) was hydrogenated at 20° in the presence of platinum oxide (200 mg.). Working up in the usual way gave the base hydrochlorides as a solid, m. p. 268—276° (424 mg.). Basification with 2N-potassium hydroxide gave an oil which partly crystallised at −20° and yielded cholestan-7α-ylamine as needles (204 mg.), m. p. *ca.* 15°, $[\alpha]_D$ −20° (*c* 1·33). The mother-liquors consisted of an uncrystallisable oil (170 mg.), $[\alpha]_D$ +54° (*c* 0·83), probably mainly the 7β-epimeride. Acetylation of cholestan-7α-ylamine with acetic anhydride–pyridine overnight gave *7α-acetamidocholestane* as needles, m. p. 216—218° (from ether), $[\alpha]_D$ +40° (*c* 0·42) [Found (after sublimation at 190°/0·01 mm.): C, 80·9; H, 11·9%].

(*b*) Cholestan-7-one oxime (1 g.) was treated with lithium aluminium hydride (250 mg.) in refluxing ether for 6 hr. The solution, worked up in the usual way, gave an oil (910 mg.) which was chromatographed on aluminium oxide (30 g.). Successive elution with ether and chloroform gave an oil (300 mg.), $[\alpha]_D$ −20° (*c* 1·0) which on acetylation with acetic anhydride in ether yielded 7α-acetamidocholestane, m. p. 216—218°, whilst use of methylene dichloride afforded an oil (610 mg.), $[\alpha]_D$ +54° (*c* 2·1), which on acetylation gave 7β-acetamidocholestane, m. p. 148—150°.

3β-Hydroxycholest-5-en-7α- and -7β-ylamine.—The amine mixture was prepared according to Eckhardt's directions [5] except that propan-1-ol was substituted for ethanol, the yield being 48%. Separation of the isomers by the method of Barnett, Ryman, and Smith [6] gave 3β-hydroxycholest-5-en-7α-ylamine, m. p. 183—185°, $[\alpha]_D$ −348° (*c* 1·6) (18%), and 3β-hydroxycholest-5-en-7β-ylamine, m. p. 196—198°, $[\alpha]_D$ +205° (*c* 1·9) (30%) (Barnett *et al.*[6] give m. p. 183—185°, $[\alpha]_D$ −327°, and m. p. 198—199°, $[\alpha]_D$ +181°, respectively).

3β-Hydroxycholestan-7α-ylamine.—3β-Hydroxycholest-5-en-7α-ylamine (1·08 g.) in acetic acid (25 c.c.) was hydrogenated at 20° in the presence of platinum oxide (300 mg.). Uptake of hydrogen was completed in 5 min. and the product on crystallisation from ether–acetone gave 3β-hydroxycholestan-7α-ylamine, m. p. 158—162°, $[\alpha]_D$ −18° (*c* 1·2) (Barnett *et al.*[6] give m. p. 87—89°, $[\alpha]_D$ −143°). Acetylation with acetic anhydride in ether at 15° gave a solid which on crystallisation from methanol furnished *7α-acetamidocholestan-3β-ol*, needles, m. p. 270—272°, $[\alpha]_D$ −9° (*c* 1·3) [Found (after drying at 120°/0·005 mm. for 4 hr.): C, 78·1; H, 11·2; N, 3·2. $C_{29}H_{51}O_2N$ requires C, 78·1; H, 11·5; N, 3·1%].

3β-Hydroxycholestan-7β-ylamine.—3β-Hydroxycholest-5-en-7β-ylamine (1·8 g.) in glacial acetic acid (43 c.c.) was shaken with hydrogen in the presence of platinum oxide (300 mg.). Uptake of hydrogen was complete in 10 min. The product was an uncrystallisable oil (1·86 g.), $[\alpha]_D$ +44° (*c* 3·0). Acetylation in ether with acetic anhydride at 15° for 16 hr. gave a solid which on crystallisation from acetone–methanol gave *7β-acetamidocholestan-3β-ol*, needles, m. p. 255—259°, $[\alpha]_D$ +63° (*c* 0·6) [Found (after drying at 120°/0·005 mm. for 4 hr.): C, 77·2; H, 11·1; N, 2·9%]. Benzoylation with benzoyl chloride–pyridine at 20° for 18 hr. gave an oil which on crystallisation form acetone gave *7β-benzamidocholestan-3β-yl benzoate*, m. p. 183—184°, $[\alpha]_D$ +31° (*c* 0·6) [Found (after drying at 90°/0·02 mm.): C, 80·7; H, 9·8. $C_{41}H_{57}O_2N$ requires C, 80·5; H, 9·4%].

3β-Hydroxycholestan-7α- and -7β-ylamine.—3β-Hydroxycholest-5-en-7-one oxime (m. p. 240—242°; 2·36 g.) in glacial acetic acid (120 c.c.) and methanol (90 c.c.) was hydrogenated in the presence of platinum oxide (317 mg.). Theoretical uptake of hydrogen was complete in 5 hr. The product, a solid, crystallised from acetone–methanol to give *3β-hydroxycholestan-7β-ylamine* which after recrystallisation from the same solvent had m. p. 184—186°, $[\alpha]_D$ +102° (*c* 0·85) (20%) [Found (after drying at 110°/0·01 mm. for 18 hr.): C, 80·4; H, 12·2; N, 3·6 $C_{27}H_{49}ON$ requires C, 80·3; H, 12·2; N, 3·5%]. Concentration of the mother-liquors gave crystals, m. p. 152—160°, which by recrystallisation from acetone gave *3β-hydroxycholestan-7α-ylamine*, m. p. 156—158°, $[\alpha]_D$ −24° (*c* 1·3) (28%) [Found (after drying at 110°/0·01 mm. for 18 hr.): C, 80·3; H, 12·2; N, 3·6%].

Cholesta-3 : 5-dien-7-one Oxime.—Cholesta-3 : 5-dien-7-one was oximated with hydroxylamine acetate in refluxing ethanol. The product on crystallisation from methanol gave cholesta-3 : 5-dien-7-one oxime as plates, m. p. 178—180°.

Cholest-4-en-7β-ylamine.—Cholesta-3 : 5-dien-7-one oxime (6 g.) in refluxing ethanol (420 c.c.) was treated with sodium (36 g.). The solution was worked up in the usual manner, and basic

material was isolated as the ether-insoluble hydrochloride, m. p. 245—252° (2·7 g.). Basification with ammonia gave cholest-4-en-7β-ylamine as an oil (2·5 g.), $[\alpha]_D$ +85° (*c* 2·8). Acetylation with acetic anhydride–pyridine at 20° for 24 hr., followed by chromatography on aluminium oxide gave, by elution with benzene–pentane (1 : 4), 7β-*acetamidocholest-4-ene*, double m. p. 150—152° and 197—198°, $[\alpha]_D$ +58° (*c* 1·43) [Found (after sublimation at 180°/0·01 mm.): C, 81·1; H, 11·5. $C_{29}H_{49}ON$ requires C, 81·3; H, 11·6%]. Benzoylation with benzoyl chloride–pyridine at 20° for 48 hr. followed by chromatography on aluminium oxide gave by elution with pentane a solid which on crystallisation from acetone afforded 7β-*benzamidocholest-4-ene* as needles, m. p. 190—192°, $[\alpha]_D$ +80° (*c* 1·12) [Found (after drying at 110°/0·01 mm. for 4 hr.): C, 83·1; H, 10·6. $C_{34}H_{51}ON$ requires C, 83·4; H, 10·5%].

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