582. B-*Nor*-5α-*cholestane*, B-*Nor*-5β-*cholestane*, *and Related Compounds*.

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Partial syntheses of B-nor-5α- and B-nor-5β-cholestane are described.

During an investigation of the stereochemistry of some B-nor-6-oxo-steroids we obtained results which required the preparation of the reference compounds B-nor-5α- and B-nor-5β-cholestane. In the literature two hydrocarbons have been reported as possessing the B-norcholestane structure, but the stereochemistry of only one of them has been examined and that not conclusively. We now describe the preparation of authentic B-nor-5α- and B-nor-5β-cholestane and thus clarify a situation which was previously confused.

Hydrogenation of either B-norcholest-5-ene or B-norcholesta-3 : 5-diene with platinum in acetic acid [1] rapidly yielded a hydrocarbon, m. p. 45°. With platinum in ether it was slow and the product a mixture from which an isomeric hydrocarbon, m. p. 80°, was isolated. No further information about the latter compound is available, but the former has been assigned both the A/B-*cis*- and the A/B-*trans*-configuration by independent workers: Fieser,[2] who prepared the hydrocarbon, m. p. 45°, $[\alpha]_D$ +10°, by reduction of Butenandt and Hausmann's diketone [3] (considered to be B-nor-5β-cholestane-3 : 6-dione) by the Wolff–Kishner method and *via* the bisethylene thioketal, gave it the *cis*-perhydroindane structure. This decision was supported by the fact that the diketone failed to isomerise at position 5 under acid or alkaline conditions, and by the relation, then generally accepted, that *cis*-perhydroindanes were more stable than their *trans*-isomers.[4] Dauben and Fonken,[5] however, favoured the alternative *trans*-structure for the low-melting hydrocarbon and prepared it by another route. Hydrogenation of B-norcholest-5-en-3β-ol (B-norcholesterol [6]) with platinum in acetic acid gave B-nor-5α-cholestan-3β-ol, oxidised to

[1] Windaus, *Ber.*, 1920, **53**, 488; cf. Lettré, *Z. physiol. Chem.*, 1933, **218**, 67.
[2] Fieser, *J. Amer. Chem. Soc.*, 1953, **75**, 4386.
[3] Butenandt and Hausmann, *Ber.*, 1937, **70**, 1154.
[4] Drieding, *Chem. and Ind.*, 1954, 992.
[5] Dauben and Fonken, *J. Amer. Chem. Soc.*, 1956, **78**, 4736.
[6] Šorm and Dykova, *Coll. Czech. Chem. Comm.*, 1948, **13**, 407.

B-nor-5α-cholestan-3-one and thence reduced by the Wolff–Kishner method to B-nor-5α-cholestane, m. p. 45—46°, $[\alpha]_D$ +11°. Their reversal of Fieser's original assignment was based on the assumption that the conformations of B-nor-5α-cholestane and 5α-cholestane were substantially identical as demonstrated by the chemical and spectral properties of the above intermediates and particularly B-nor-5α-cholestan-3β-ol. Our suspicions that Dauben and Fonken's B-nor-5α-cholestan-3-one was an A/B-*cis*-compound were confirmed by the measurement by Djerassi, Marshall, and Nakano [7] of its optical rotatory dispersion. This present work supports this observation and places on a firmer basis the stereochemistry at position 5 of the B-nor-compounds described above.

Catalytic hydrogenation of 3β-acetoxy-B-norcholest-5-ene (I; R = Ac) with platinum–acetic acid occurred rapidly to give, after hydrolysis, a mixture of two alcohols, double m. p. 58—60° and 76—77°, $[\alpha]_D$ +16° (81%), and m. p. 132°, $[\alpha]_D$ −9° (16%), which from their relative ease of elution from alumina were considered to be B-nor-5β- (II; R = H) and B-nor-5α-cholestan-3β-ol (V; R = H) respectively. (Dauben and Fonken [5] record m. p. 77—78° and $[\alpha]_D$ −30·8° for B-nor-5α-cholestan-3β-ol, and m. p. 62—64° and $[\alpha]$ −9·8° for B-nor-5α-cholestan-3-one although the specific rotations calculated from their own molecular-rotation data are respectively +16° and +19°.) A similar result was obtained with platinum–ethyl acetate–perchloric acid, but in ethyl acetate alone no hydrogenation occurred. Addition of a little acetic acid as promoter caused slow uptake of hydrogen and the yield of alcohol (V) was increased to 47%. These results recall the influence of solvent on the stereochemical course of reduction of Δ^4- and Δ^5-steroids,[8,9] and bear comparison with the results of hydrogenation of A-norcholest-3-enes [10,11] and Δ^{14}-steroids.[12] In acid solution 3-methyl-A-norcholest-3-ene and its unmethylated homologue give mixtures, whereas normal reduction of a 14 : 15-double linkage yields C/D-*trans*-steroids although the epimeric C/D-*cis*-compound can be formed when α-orientated bulky neighbouring groups are present at, *e.g.*, position 17 (ref. 13) or even 11 (ref. 14).

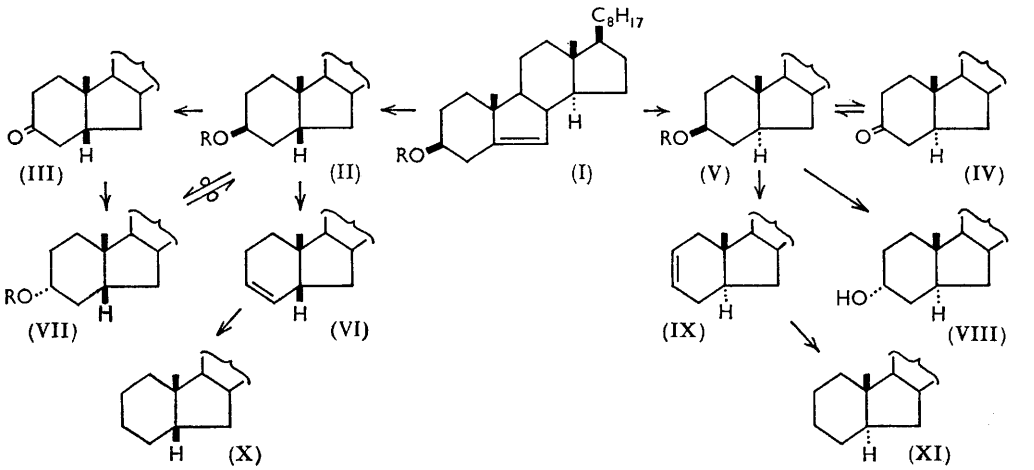
Oxidation of the alcohol (II; R = H) with chromium trioxide in pyridine gave B-nor-5β-cholestan-3-one (III), the structure of which was confirmed by reduction to B-nor-5β-cholestan-3α-ol (VII; R = H) in quantitative yield by lithium aluminium hydride. The production of the 3α-alcohol is contrary to Dauben and Fonken's result,[5] but consistent with the reduction of 3-oxo-A/B-*cis*-steroids by metal hydrides.[15] With " unhindered " ketones of this type where approach of the aluminium hydride ion can occur with equal facility from either face of the molecule, the product is determined by the relative stability of the two possible intermediate transition states and thus reduction of a 3-oxo-A/B-*cis*-steroid yields predominantly the equatorial 3α-alcohol.

The 3α-alcohol (VII; R = H) was also obtained by acetolysis of B-nor-5β-cholestan-3β-yl toluene-*p*-sulphonate (II; R = $C_6H_4Me{\cdot}SO_2$), followed by hydrolysis and chromatography of the product. In this solvolysis the alcohol (VII; R = H) was accompanied by an oily hydrocarbon which we consider to be B-nor-5β-cholest-3-ene (VI) by analogy with the behaviour shown by 5β-cholestan-3α-yl and -3β-yl toluene-*p*-sulphonate under identical conditions.[16] Replacement reactions of saturated steroid 3α- and 3β-yl toluene-*p*-sulphonates on aluminium oxide [17] reproduce qualitatively the results (inversion and

[7] Djerassi, Marshall, and Nakano, *J. Amer. Chem. Soc.*, 1958, **80**, 4853.
[8] Agashe, Shoppee, and Summers, *J.*, 1957, 3107.
[9] Lewis and Shoppee, *J.*, 1955, 1365.
[10] Lettré, *Z. physiol. Chem.*, 1933, **221**, 73.
[11] Schmid and Kägi, *Helv. Chim. Acta*, 1950, **33**, 1581; Shoppee and Summers, *J.*, 1952, 2528.
[12] For many references see Lettré, Inhoffen, and Tschesche, " Sterine, Gallensauren and verwandte Naturstoffe," Enke, Stuttgart, 1954, Vol. I, p. 287 *et seq.*
[13] Speiser and Reichstein, *Helv. Chim. Acta*, 1947, **30**, 2143; 1948, **31**, 623.
[14] Meyer, *ibid.*, 1949, **32**, 1599.
[15] Shoppee and Summers, *J.*, 1950, 687; Dauben, Fonken, and Knoyle, *J. Amer. Chem. Soc.*, 1956, **78**, 2579; Dauben, Blanz, Jiu, and Micheli, *ibid.*, p. 3752; Wheeler and Mateos, *Canad. J. Chem.*, 1958, **36**, 1431; see also criticisms by Hardy and Wicker, *J. Amer. Chem. Soc.*, 1958, **80**, 640.
[16] Shoppee, *J.*, 1946, 1138; Bridgewater and Shoppee, *J.*, 1953, 1709.
[17] Chang and Blickerstaff, *Chem. and Ind.*, 1958, 590.

elimination) of bimolecular hydrolysis in solution,[16] and we find that chromatography of the toluene-*p*-sulphonate (VII; R = $C_6H_4Me{\cdot}SO_2$) on basic alumina gives B-nor-5β-cholest-3-ene (VI) and the 3β-alcohol (II; R = H). The parent hydrocarbon B-nor-5β-cholestane (X) was obtained by (*a*) reduction of the toluene-*p*-sulphonates (II and VII; R = $C_6H_4Me{\cdot}SO_2$) with lithium aluminium hydride and (*b*) catalytic hydrogenation of B-nor-5β-cholest-3-ene (VI).

The same reactions applied to B-nor-5α-cholestan-3β-ol (V; R = H), and similarly interpreted, support the correctness of its formulation as an A/B-*trans*-compound. Oxidation with chromium trioxide in pyridine gave B-nor-5α-cholestan-3-one (IV) which by



reduction with lithium aluminium hydride or sodium in propanol regenerated the 3β-alcohol (V; R = H) in accord with a 3-oxo-A/B-*trans*-structure for the ketone (IV).[15] The epimeric 3α-alcohol (VIII) was prepared for comparison by chromatography of B-nor-5α-cholestan-3β-yl toluene-*p*-sulphonate (V; R = $C_6H_4Me{\cdot}SO_2$) on basic alumina. Reduction of this ester with lithium aluminium hydride yielded B-nor-5α-cholestane (XI), also prepared by hydrogenation of a hydrocarbon assumed by analogy * with the similar behaviour of 5α-cholestan-3β-yl toluene-*p*-sulphonate to be B-nor-5α-cholest-2-ene (XI), which was the principal product of the chromatographic decomposition of the ester (V; R = $C_6H_4Me{\cdot}SO_2$).

Our stereochemical assignments are supported by the optical rotatory dispersion curves of the ketones (III and IV). The asymmetric environment of a carbonyl group in a cyclic system is reflected in its rotatory dispersion curve which thus detects conformational changes. The ketones (III and IV) in methanol gave single Cotton-effect curves [19] respectively negative and positive (amplitudes expressed as molecular rotations, −6000° and +7300°). These values may be compared with values of −2700° and 6500° for 5β- and 5α-cholestan-3-one respectively,[20] and on the basis of simple analogy the data support the allotment of the configurations given here to the B-nor-ketones [cf. Djerassi, Marshall, and Nakano,[7] who measured the 5β-B-nor-compound only; our values for (III) agree closely with theirs]. Consideration of the rotation data in the light of the " octant rule " confirms this allotment.[21]

* Hydrocarbon (IX) could possibly be B-nor-5α-cholest-3-ene since it seems that extra strain in ring B can influence the relative reactivities of positions 2 and 4, *e.g.*, methylation of 5α-cholest-7-en-3-one gives the 4α-methyl and not the expected 2α-methyl compound.

[18] Wells and Neiderhiser, *J. Amer. Chem. Soc.*, 1957, **79**, 6569; Mazur and Sondheimer, *ibid.*, 1958, **80**, 6296.
[19] For nomenclature see Djerassi and Klyne, *Proc. Chem. Soc.*, 1957, 55.
[20] Djerassi, Riniker, and Riniker, *J. Amer. Chem. Soc.*, 1956, **78**, 6362.
[21] Personal communication from Dr. W. Klyne.

Dauben and Fonken [5] consider that the infrared spectra of their alcohol and its acetate further support its formulation as B-nor-5α-cholestan-3β-ol. Since the alcohol displayed bands at 1040 and 1076 cm.$^{-1}$, and the acetate a single strong band at 1242 cm.$^{-1}$, they concluded by analogy that these were consistent with the presence of an equatorial hydroxyl group and an A/B-*trans* ring junction. The Table gives the frequencies of the principal absorption bands found in the range 990—1050 cm.$^{-1}$ for the epimeric pairs of cholestan-3-ols and B-norcholestan-3-ols. The latter also gave bands of low intensity in the 1070—1090 cm.$^{-1}$ region.

Frequencies (cm.$^{-1}$) of the intense bands in the range 990—1050 cm.$^{-1}$ (in carbon disulphide) for 3α- and 3β-hydroxycholestanes and β-norcholestanes.

Equatorial		*Axial*	
5α-Cholestan-3β-ol	1038	5α-Cholestan-3α-ol	1002
B-Nor-5α-cholestan-3β-ol	1048, 1009	B-Nor-5α-cholestan-3α-ol	1048, 1009, 998
5β-Cholestan-3α-ol	1038	5β-Cholestan-3β-ol	1034
B-Nor-5β-cholestan-3α-ol	1047	B-Nor-5β-cholestan-3β-ol	1042

In saturated steroids an equatorial 3-hydroxyl group gives a strong band due to the C–O stretching vibration near 1040 cm.$^{-1}$: an axial group absorbs at a lower frequency usually in the range 1000—1040 cm.$^{-1}$.[22] The absorption bands for the B-nor-5β-cholestan-3-ols conform to this pattern, the higher frequency being probably attributable to distortion of ring A by fusion with a cyclopentane ring. The spectra for the B-nor-5α-cholestan-3-ols are more complex owing to the presence of additional more intense bands about 1000 cm.$^{-1}$ which on the basis of simple analogy are difficult to interpret with certainty. Thus although conclusions as to the stereochemistry on the basis of analogy with spectral details of the cholestan-3-ols can be drawn, we feel that until further information about perhydroindanols of this type becomes available interpretation must be made with caution.

This work supports the original findings of Fieser [2] and leads to the conclusion that the most stable conformation of B-nor-steroids features an A/B-*cis*-ring fusion. Thus reduction of B-norcholest-4-en-3-one by lithium–ammonia,[5] a reagent which usually yields the thermodynamically more stable product,[23] gives B-nor-5β-cholestan-3-one (III). Also zinc–acetic acid reduction of B-norcholest-4-ene-3,6-dione [2,5] and 3-oxo-6,7-secocholest-4-ene-6,7-dioic acid [2] afford the 5β-isomers. It has recently been reported that catalytic reduction of 3β-hydroxy-B-norandrost-5-en-17-one yields 3β-hydroxy-B-nor-5α-androstan-17-one;[24] we feel this hydrogenation should be reconsidered in the light of the above experiments.

We wish to defer at present a detailed analysis of the conformations of these perhydroindanes and the related C-nor-D-homosteroids until information about the B/C-ring union becomes available.

Experimental

Infrared spectra were recorded on a Grubb–Parsons GS2 double-beam grating spectrometer. $[\alpha]_D$ are in chloroform.

B-*Nor*-5β- *and* B-*Nor*-5α-*cholestan*-3β-*ol*.—(*a*) 3β-Acetoxy-B-norcholest-5-ene {m. p. 79°, $[\alpha]_D$ −84° (*c* 1·1); 1·14 g.} was hydrogenated with platinum oxide (184 mg.) in acetic acid (80 ml.); the oily product was hydrolysed with 5% ethanolic potassium hydroxide (50 ml.) for 1 hr. and the resulting oil chromatographed on aluminium oxide (40 g.). Elution with ether (6 × 100 ml.) gave an oil (827 mg.) which on crystallisation from methanol gave B-*nor*-5β-*cholestan*-3β-*ol*, double m. p. 56—60° and 74—76°, $[\alpha]_D$ +17° (*c* 1·6) (Found: C, 83·5; H, 12·4. $C_{26}H_{46}O$ requires C, 83·35; H, 12·4%). Further elution with ether (4 × 100 ml.) gave B-*nor*-5α-*cholestan*-3β-*ol* (162 mg.), m. p. 132° (needles from acetone), $[\alpha]_D$ −9° (*c* 1·7) (Found: C, 83·1; H, 12·5%).

[22] Jones and Roberts, *J. Amer. Chem. Soc.*, 1958, **80**, 6121 and references there cited.
[23] Barton and Robinson, *J.*, 1954, 3045; Birch and Smith, *Quart. Reviews*, 1958, **12**, 17,
[24] Joska and Šorm, *Coll. Czech. Chem. Comm.*, 1958, **23**, 1377; Joska, Fajkos, and Šorm, *Chem. and Ind.*, 1958, 1665.

(*b*) 3β-Acetoxy-B-norcholest-5-ene (2·3 g.) in ethyl acetate (40 ml.) containing 60% perchloric acid (6 drops) was shaken with platinum oxide (200 mg.) in hydrogen until absorption ceased (20 min.). Working up as above followed by chromatography on aluminium oxide (100 g.) gave B-nor-5β-cholestan-3β-ol (1·95 g.), double m. p. 58—60° and 76—77°, [α] +16° (*c* 1·1), and B-nor-5α-cholestan-3β-ol (318 mg.), m. p. 131—132°.

(*c*) B-Nor-cholest-5-en-3β-ol {m. p. 116°, $[\alpha]_D$ −90° (*c* 1·0); 2·1 g.} in ethyl acetate (50 ml.) shaken with platinum oxide (200 mg.) failed to take up hydrogen. Absorption of hydrogen occurred slowly after the addition of acetic acid (12 drops) and was complete after 12 hr. Chromatography of the product gave B-nor-5β-, double m. p. 56—60° and 74° (1·03 g.), and -5α-cholestan-3β-ol, m. p. 129—131° (989 mg.).

B-*Nor*-5β-*cholestan*-3β-*yl Toluene*-p-*sulphonate*.—B-Nor-5β-cholestan-3β-ol (1·5 g.) in pyridine (15 ml.) was treated with toluene-*p*-sulphonyl chloride (1·5 g.) and left overnight. After the usual working up the *toluene*-p-*sulphonate* crystallised from ether as needles, m. p. 110—112°, $[\alpha]_D$ +10° (*c* 1·5) (Found: C, 75·2; H, 9·5. $C_{33}H_{52}O_3S$ requires C, 75·0; H, 9·9%).

B-*Nor*-5β-*cholestane*.—(*a*) The above toluene-*p*-sulphonyl ester (400 mg.) in ether (100 ml.) was heated under reflux with lithium aluminium hydride for 24 hr. The product, an oil, was chromatographed on aluminium oxide (15 g.). Elution with pentane (2 × 40 ml.) gave B-nor-5β-cholestane (259 mg.), m. p. 42—45°, $[\alpha]_D$ +8° (*c* 1·5) (from acetone), and elution with chloroform gave B-nor-5β-cholestan-3β-ol, m. p. 75—76° (49 mg.).

(*b*) B-Nor-5β-cholest-3-ene (157 mg.) in ethyl acetate containing 60% perchloric acid (4 drops) was hydrogenated in the presence of platinum oxide (50 mg.). The oily product crystallised from acetic acid to give B-nor-5β-cholestane, m. p. 45°, $[\alpha]_D$ +10° (*c* 1·0).

B-*Nor*-5β-*cholestan*-3-*one*.—B-Nor-5β-cholestan-3β-ol (1 g.) in pyridine (10 ml.) was treated with chromium trioxide (1 g.) in pyridine (10 ml.) and left overnight. After dilution with pentane the solution was filtered, and the filtrate evaporated in a vacuum. The oily product was chromatographed on aluminium oxide (30 g.). Elution with benzene–pentane (1 : 9; 6 × 100 ml.) gave B-*nor*-5β-*cholestan*-3-*one* (539 mg.), m. p. 68—70°, $[\alpha]_D$ +18·5° (*c* 1·2), $\nu_{max.}$ 1715 cm.$^{-1}$ in carbon tetrachloride (Found: C, 83·7; H, 11·75. $C_{26}H_{44}O$ requires C, 83·8; H, 11·9%). Elution with ether gave starting material (403 mg.). Rotatory dispersion in methanol (*c* = 0·1): [*M*] = −40 at 600 mμ; −1830 at 310 mμ (trough); +4080 at 265 mμ.

B-*Nor*-5β-*cholestan*-3α-*ol*.—(*a*) B-Nor-5β-cholestan-3-one (300 mg.) in ether (20 ml.) was left for 2 hr. at room temperature with lithium aluminium hydride (300 mg.). The oily product was chromatographed on aluminium oxide (20 g.). Elution with ether–benzene (1 : 1; 11 × 25 ml.) gave an oil (287 mg.) which crystallised. Crystallisation from a solvent was difficult and B-*nor*-5β-*cholestan*-3α-*ol* was obtained as an amorphous material, m. p. 89—92° (from ethyl acetate), $[\alpha]_D$ +9·5° (*c* 1·7) (Found: C, 83·2; H, 12·3. $C_{26}H_{46}O$ requires C, 83·35; H, 12·4%). The *toluene*-p-*sulphonate*, prepared in the usual way, crystallised from pentane as needles, m. p. 96—100°, $[\alpha]_D$ +17° (*c* 1·6) (Found: C, 74·6; H, 9·9. $C_{33}H_{52}O_3S$ requires C, 74·96; H, 10·0%).

(*b*) B-Nor-5β-cholestan-3β-yl toluene-*p*-sulphonate (879 mg.) in acetic acid (25 ml.) containing anhydrous potassium acetate (6 g.) was heated at 95° for 2·5 hr. The oily product was treated with lithium aluminium hydride in ether for 0·5 hr. The product was chromatographed on basic aluminium oxide (Woelm; 30 g.). Elution with pentane (2 × 100 ml.) gave B-nor-5β-cholest-3-ene (404 mg.) as an oil, $[\alpha]_D$ +20° (*c* 2·2); and elution with chloroform gave B-nor-3β-cholestan-3α-ol (214 mg.) which separated from ethyl acetate as hair-like crystals, m. p. 86—88°, $[\alpha]_D$ +12° (*ca.* 2·0). The infrared spectra of the two specimens were identical.

B-*Nor*-5β-*cholestan*-3β-*ol*.—B-Nor-5β-cholestan-3α-yl toluene-*p*-sulphonate (810 mg.) in benzene was adsorbed on basic alumina (Woelm) and left 4 days. Elution with pentane gave B-*nor*-5β-*cholest*-3-*one* (266 mg.) as an oil which crystallised with difficulty from acetone and then had m. p. 28—30°, $[\alpha]_D$ +7° (*c* 2·7) (Found: C, 87·3; H, 12·4. $C_{26}H_{44}$ requires C, 87·6; H, 12·4%). Elution with chloroform gave B-nor-5β-cholestan-3β-ol (247 mg.), m. p. and mixed m. p. 74—77°.

B-*Nor*-5α-*cholestan*-3β-*yl Toluene*-p-*sulphonate*.—B-Nor-5α-cholestan-3β-ol (700 mg.) in pyridine (10 ml.) was treated with toluene-*p*-sulphonyl chloride (650 mg.) and left for 2 days. The *toluene*-p-*sulphonate* crystallised from ether as needles, m. p. 123—125°, $[\alpha]_D$ −22° (*c* 2·0) (Found: C, 75·2; H, 9·6. $C_{33}H_{52}O_3S$ requires C, 74·96; H, 9·9%).

B-*Nor*-5α-*cholestane*.—(*a*) The last toluene-*p*-sulphonate (90 mg.) in ether (10 ml.) was heated overnight with lithium aluminium hydride (250 mg.). Filtration of a pentane solution of the product through aluminium oxide followed by removal of the solvent gave B-nor-5α-cholestane,

m. p. 78—79° (needles from acetone), $[\alpha]_D$ +9° (*c* 0·9) (Found: C, 87·1; H, 13·0. $C_{26}H_{46}$ requires C, 87·1; H, 12·9%].

(*b*) B-Nor-5α-cholest-2-ene (105 mg.) in ether (5 ml.) and acetic acid (5 ml.) was hydrogenated in the presence of platinum oxide (20 mg.). The product crystallised from acetone to give B-nor-5α-cholestane as needles, m. p. 78—80°.

B-*Nor*-5α-*cholestan*-3-*one*.—B-Nor-5α-cholestan-3β-ol (312 mg.) in pyridine (6 ml.) was treated with chromium trioxide (400 mg.) and left overnight. After dilution with pentane the solution was filtered and the filtrate evaporated under reduced pressure. The crystalline product was chromatographed on aluminium oxide (10 g.). Elution with benzene–pentane (1 : 4) gave B-*nor*-5α-*cholestan*-3-*one*, m. p. 98—99° (from methanol), $[\alpha]_D$ +25·5° (*c* 0·75), $\nu_{max.}$ 1706 cm.$^{-1}$ (in carbon tetrachloride) (Found: C, 83·5; H, 12·0. $C_{26}H_{44}O$ requires C, 83·8; H, 11·9%). Rotatory dispersion in methanol (*c* = 0·1): [*M*] = 0 at 600 mμ; +3470 at 310 mμ (peak); −3790 at 260 mμ.

Reduction of the ketone with lithium aluminium hydride in ether gave in quantitative yield B-nor-5α-cholestan-3β-ol, m. p. and mixed m. p. 130—131° (from methanol), $[\alpha]_D$ −10° (*c* 0·96).

B-*Nor*-5α-*cholestan*-3α-*ol*.—B-Nor-5α-cholestan-3β-yl toluene-*p*-sulphonate (850 mg.) in benzene was adsorbed on basic aluminium oxide (Woelm) and left for one week. Elution with pentane gave B-*nor*-5α-*cholest*-2-*ene* (326 mg.), m. p. 82—84° (plates from acetone), $[\alpha]_D$ +30·6° (*c* 1·5) (Found: C, 87·4; H, 12·1. $C_{26}H_{44}$ requires C, 87·6; H, 12·4%). Elution with chloroform gave B-*nor*-5α-*cholestan*-3α-*ol* (225 mg.), m. p. 124—127° (needles from acetone), $[\alpha]_D$ −24° (*c* 1·07) (Found: C, 83·5; H, 12·1. $C_{26}H_{46}O$ requires C, 83·35; H, 12·4%). Admixture with B-nor-5α-cholestan-3β-ol gave m. p. 116—119°.

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