SYNTHESIS OF 2-OXYGENATED 4,5-CYCLO-A-HOMO-B-NORCHOLESTANE DERIVATIVES*

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Synthesis of 2-oxygenated 4α,5-cyclo-A-homo-B-nor-5α-cholestane derivatives is described and structure of the compounds established by chemical and spectral means.

In our previous paper[1] we delt with syntheses of the two isomeric 4,5-cyclo-A-homo--B-norcholestanes which represented a new type of modified steroid system, and prepared some compounds with oxygen function at $C_{(3)}$. In this paper we present a continuation of these studies and describe syntheses of some 2-oxygenated 4α,5--cyclo-A-homo-B-norcholestane derivatives, as well as the isomeric 2,3-epoxides.

We set out from the previously described[1] bromo ketone *III* which was prepared by bromination of the enolacetate *II*. This method proved superior to the formerly described direct bromination. Hydride reduction afforded the known[1] bromohydrins *IV* and *V* the structure of which has also been established by us. Both bromohydrins were transformed to the olefin *VI* with zinc dust in ethanol. Peracid oxidation yielded a mixture of the epoxides *IX* and *X* in which – according to the TLC – the α-isomer slightly predominated. Reductive cleavage of these epoxides with lithium aluminium hydride in tetrahydrofuran did not proceed stereospecifically and, in each case, both 2-hydroxy and 3-hydroxy derivatives of the corresponding configuration have been formed. In the β-series the 2β-alcohol *XI* represented the main product, in contrast to the α-series, where both alcohols *XIV* and *XV* have been isolated in about equal quantities. The steric course of this reaction reflects the conformational situation in these four alcohols and similar information may be obtained from the ^{1}H-NMR evidence: We have shown in our previous paper that the 3β-hydroxyl in this system is equatorial and 3α-hydroxyl is axial. On the other hand, in the 2-hydroxy derivatives *XI* and *XIV* the width of the multiplets of the $C_{(2)}$-protons (30 Hz and 31 Hz) points to their axial conformation. Thus both hydroxyls at $C_{(2)}$ are equatorial and in each of the 2-hydroxy derivatives the A-ring has different conformation. This is probably a consequence of a nonbonded interaction between the

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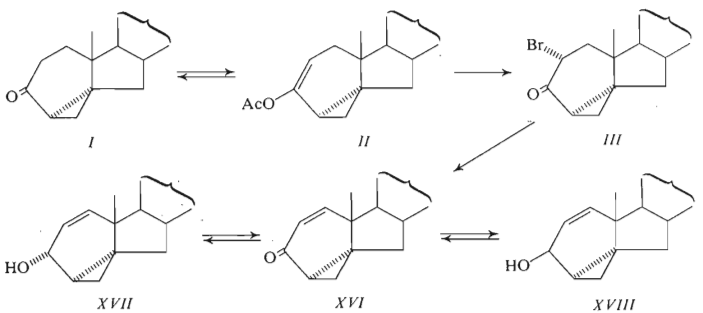
2β-hydroxyl and $C_{(10)}$-methyl group which forces the A ring into a conformation in which the 2β-bond is equatorial. Fig. 1 shows this anomalous conformation of ring A in the 2β-alcohol *XI* in comparison with the conformation of this ring in the 2α- and both $C_{(3)}$-epimeric alcohols *XIII* and *XV* (Fig. 2). An analogous situation exists in the 4α,5-cyclosteroids of the normal series, as observed Černý and coworkers[2].



I *II* *III*

XVII *XVI* *XVIII*

Alcohols *XI* and *XIV* gave on chromic acid oxidation the 2-oxo derivative *VII* which also was obtained from the epoxide *IX* by BF_3-etherate. Bromination with Jacques' reagent yielded the bromoketone *VIII*. Structure of this compound follows from spectral evidence: ^{1}H-NMR shows clearly that the bromine atom is located at $C_{(1)}$ (singlet at 3·96 ppm). CD curve of the ketone *VII* shows positive effect, in the ketone *VIII* a strong negative effect, and the carbonyl frequency in IR is shifted by $+7\ cm^{-1}$ in the bromo ketone *VIII* when compared with the parent ketone *VII*.

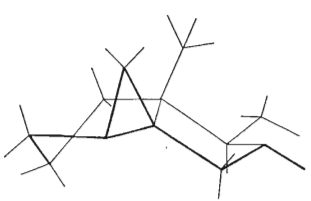
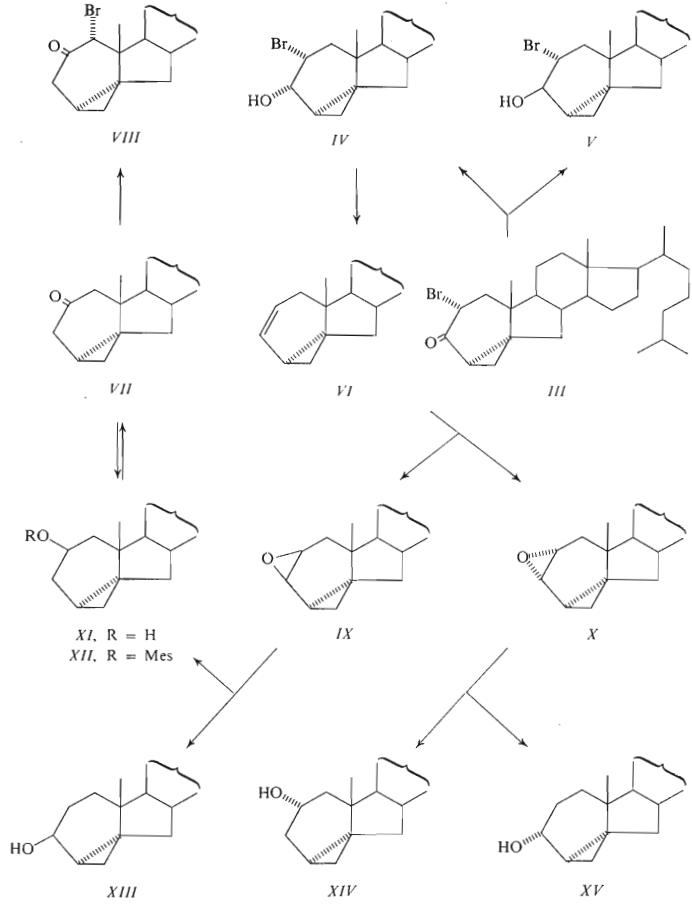


FIG. 1
Conformation of Ring A in the 2β-Hydroxy Derivative *XI*

FIG. 2
Conformation of Ring A in the 2α-Hydroxy Derivative *XIV*



Positive value of the CD curve in the unbrominated ketone is consistent only with the conformation presented by Fig. 3. Bromination changed direction of the molecular ellipticity and the CD curve of the bromo ketone *VIII* shows a strong negative

effect. The bromine is thus located in the negative octant of the octant projection, has axial conformation and therefore α-configuration. The carbonyl shift in IR region ($+7\ cm^{-1}$) is also in agreement with the axial conformation of the halogen[3].

Further, the allylic alcohols *XVII* and *XVIII* were of interest as potential starting compounds for syntheses of new types of cyclo steroids. The bromo ketone *III* afforded on reaction with collidine the unsaturated ketone *XVI* which on hydride reduction gave the desired epimeric alcohols *XVII* and *XVIII*. Both were oxidised with Jones' reagent back to the starting unsaturated ketone *XVI*.

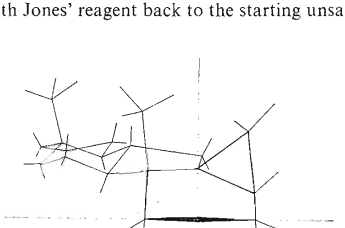


FIG. 3
Octant Projection of the A Ring in the Bromo Ketone *VIII*

EXPERIMENTAL

Melting points were determined on a Kofler block. Analytical samples were dried at 80°C/0·2 Torr. Optical measurements were carried out in chloroform with an error of ±1°. The infrared spectra were recorded on the Zeiss UR 10 spectrometer in tetrachloromethane unless otherwise stated. The ^{1}H-NMR spectra were recorded on the Varian HA-100 instrument in chloroform and corrected to tetramethylsilane (7·25 ppm) unless otherwise stated. The chemical shift is given in ppm. The identity of samples prepared by different routes was checked by mixture melting point determination, by thin-layer chromatography (TLC), and by infrared spectra. Ligroin of b.p. 40—60°C was used as solvent. Working up of an ethereal solution means extraction with 5% hydrochloric acid, water, 5% sodium hydrogen carbonate, water, drying with magnesium sulphate, and evaporation of the solvent.

4α,5-Cyclo-A-homo-B-nor-5α-cholestan-3-one (*I*)

A solution of the enol acetate *II* (100 mg) in methanol (50 ml) was treated with potassium hydroxide (50 mg) in methanol (3 ml) and allowed to stand at room temperature for 10 minutes. The excess alkali was removed with acetic acid, methanol distilled off under reduced pressure, and the residue was diluted with water. The steroid was isolated with ether, the ethereal solution was washed with potassium hydrogen carbonate, dried, and ether removed. The product was chromatographed on a silica gel column (5 g) in benzene to yield after working up of the corresponding fractions and crystallisation from methanol 45 mg of the ketone *I*, m.p. 147—148°C, $[\alpha]_D^{20}$ −17° (*c* 1·32) in agreement with the literature[1].

3-Acetoxy-4α,5-cyclo-A-homo-B-nor-5α-cholest-2-ene (*II*)

The ketone *I* (1·5 g) in isopropenyl acetate (45 ml) was treated with a solution of conc. sulphuric acid (3 drops) in isopropenyl acetate (6 ml) and 25 ml of the solvent were distilled off within 2 h. Fresh catalyst and isopropenyl acetate (45 ml) were added and 25 ml of the solvent were collected similarly. The rest of the solvent was then removed under reduced pressure, the residue was dissolved in benzene–ligroin (1 : 1) and filtered over alumina (alk. act. III). The residue after evaporation of the solvent was chromatographed on a silica gel column (80 g) in ligroin–benzene (2 : 3). The corresponding fractions were combined, solvent removed and the residue was crystallised from ether–methanol to yield 1·16 g of the enol acetate *II*, m.p. 46–47°C $[\alpha]_D^{20}$ +4·5°C, (*c* 1·43). IR: 3080 (cyclopropane), 1762, 1223, 1022 cm^{-1} (enol acetate). For $C_{29}H_{46}O_2$ (426·7) calculated: 81·63% C, 10·87% H; found: 81·80% C, 10·70% H.

2α-Bromo-4α,5-cyclo-A-homo-B-nor-5α-cholestan-3-one (*III*)

The enol acetate *II* (380 mg) in tetrachloromethane (10 ml) was treated at 0°C under stirring with a solution of bromine (0·05 ml) in the same solvent (1 ml). The mixture was diluted with ether, the solution was washed with a sodium thiosulphate solution, then with 5% sodium hydrogen carbonate and water, dried, and the solvent was removed. The residue was chromatographed over silica gel (30 g) in ligroin–benzene (3 : 2). Working up of the corresponding fractions and crystallisation from methanol gave 130 mg of the bromo ketone *III*, m.p. 159–160°C, $[\alpha]_D^{20}$ −14° (*c* 1·20) in accordance with the literature[1].

4α,5-Cyclo-A-homo-B-nor-5α-cholest-2-ene (*VI*)

a) *From* 2α-*bromo*-4α,5-*cyclo*-A-*homo*-B-*nor*-5α-*cholestan*-3α-*ol* (IV): The bromohydrin[1] *IV* (250 mg) in ethanol (20 ml) was refluxed with zinc dust (1·25 g) for 4 h. The metal was filtered off, ethanol removed under reduced pressure, and the residue was dissolved in ether. The ethereal solution was worked up the product dissolved in ligroin and chromatographed over silica gel (10 g) in the same solvent. The corresponding fractions were worked up, and the residue crystallised from methanol–ether to yield 140 mg of the olefin *VI*, m.p. 74–75°C, $[\alpha]_D^{20}$ −32° (*c* 1·33). IR: 3060, 3025, 1652, 1644, 701 cm^{-1}. ^{1}H-NMR: 0·45 (t, $J_{gem} = J_{vic} = 4·5$ Hz, one cyclopropane proton), 0·68 (s, 18-H), 0·80 (s, 19-H), 0·86 (d, $J = 6·5$ Hz, 26- and 27-H), 0·91 (d, $J = 6$ Hz, 21-H), 5·41 (d of triplets, $J_{2,3} = 9·7$ Hz, $J_{2,1A} = J_{2,1B} = 4·4$, 2-H), 5·90 (d of pentets, $J_{3,2} = 9·7$ Hz, $J_{3,4} = 3·8$ Hz, $J_{3,1A} = J_{3,1B} = 1·8$ Hz, 3-H). For $C_{27}H_{44}$ (368·6) calculated: 87·97% C, 12·03% H; found; 87·87% C, 12·15% H.

b) *From* 2α-*bromo*-4α,5-*cyclo*-A-*homo*-B-*nor*-5α-*cholestan*-3β-*ol* (V): The bromohydrin *V* (100 mg) in ethanol (15 ml) was treated with zinc dust as described in the foregoing experiment. Similar working up and crystallisation from methanol–ether gave 60 mg of the olefin *VI*, m.p. 73–74°C, identical with the compound prepared as under *a*).

4α,5-Cyclo-A-homo-B-nor-5α-cholestan-2-one (*VII*)

a) *From* 4α,5-*cyclo*-A-*homo*-B-*nor*-5α-*cholestan*-2β-ol (XI): The alcohol *XI* (300 mg) in acetone (15 ml) was treated with excess Jones reagent. After 10 minutes at room temperature the oxidising agent was removed with methanol, the mixture was diluted with water, and the solid was collected. The product was dissolved in ether, the ethereal solution was washed with 5% sodium hydrogen carbonate, dried, and ether removed. The residue was crystallised from methanol to yield 210 mg of the ketone *VII*, m.p. 102–103°C, $[\alpha]_D^{20}$ +85° (*c* 1·29). Mass spectrum: M^+ 384.

IR: 3060 (cyclopropane), 1713 cm^{-1} (carbonyl). ^{1}H-NMR: 0·32 (t, $J = 5$ Hz, one cyclopropane proton), 0·685 (s, 18-H), 0·765 (s, 19-H), 0·875 (d, $J = 6$ Hz, 26- and 27-H), 0·935 (d, J 6 Hz, 21-H), 2·28 (d, $J_{1,1} = 15$ Hz, 1-H), 2·58 (dd, $J_{3,3} = 16$ Hz, $J_{3,4} = 7$ Hz, 3-H). For $C_{27}H_{44}O$ (384·6) calculated: 84·31% C, 11·53% H; found: 84·73% C, 11·72% H.

b) *From* 4α,5-*cyclo*-A-*homo*-B-*nor*-5α-*cholestan*-2α-*ol* (XIV): The alcohol *XIV* (20 mg) was oxidised with Jones' reagent in acetone (1·5 ml) as described in the previous experiment. Working up and crystallisation from methanol afforded 12 mg of the ketone *VII*, m.p. 101–102°C, $[\alpha]_D^{20}$ +83° (*c* 0·76), identical with the compound prepared as under *a*).

c) *From* 2β,3β-*epoxy*-4α,5-*cyclo*-A-*homo*-B-*nor*-5α-*cholestane* (IX): The epoxide *IX* (150 mg) in ether (6 ml) was treated with boron trifluoride etherate (0·02 ml) and allowed to stand at room temperature for 20 minutes. The mixture was diluted with ether, washed with 5% sodium hydrogen carbonate, water, dried, and ether removed. The residue was chromatographed over silica gel (15 g) in ligroin–benzene (2 : 1). Working up and crystallisation from methanol yielded 30 mg of the ketone *VII*, m.p. 101–102°C, $[\alpha]_D^{20}$ +82° (*c* 1·25), identical with the compound prepared as under *a*).

1α,Bromo-4α,5-cyclo-A-homo-B-nor-5α-cholestan-2-one (*VIII*)

The ketone *VII* (340 mg) in tetrahydrofuran (3·5 ml) was treated with Jacques' reagent (350 mg). After 5 minutes at room temperature the mixture was diluted with ether, the ethereal solution was washed with a sodium thiosulphate solution, with 5% sodium bicarbonate, water, dried, and ether was removed. The product was chromatographed over silica gel (30 g) in ligroin–benzene (9 : 1). Fractions with the lipophilic product were combined, solvent removed, and the residue was crystallised from methanol to yield 40 mg of the bromo ketone *VIII*, m.p. 98–99°C, $[\alpha]_D^{20}$ −60° (*c* 1·34). Mass spectrum: M^+ 463. IR: 3065 (cyclopropane), 1720 cm^{-1} (carbonyl). ^{1}H-NMR: −0·05 to +0·60 (multiplet of two cyclopropane protons), 0·62 (s, 18-H and 19-H), 0·99 (d, $J = 6$ Hz, 26-H and 27-H), 1·03 (d, $J = 6$ Hz, 21-H), 2·07 and 3·40 (d, and dd, 3-H). For $C_{27}H_{43}BrO$ (463·5) calculated: 69·95% C, 9·35% H, 17·25% Br; found: 69·71% C, 9·18% H, 17·65% Br.

2β,3β-Epoxy-4α,5-cyclo-A-homo-B-nor-5α-cholestane (*IX*)

The olefin *VI* (250 mg) in ether (5 ml) was treated with a solution of chloroperbenzoic acid (150 mg) in ether (3 ml) and allowed to stand at room temperature for 20 h. The mixture was diluted with ether, the excess peracid was extracted with 5% sodium carbonate, the ethereal solution was washed with water, dried, and ether distilled off. The residue was chromatographed over silica gel (50 g) in benzene. Fractions with the lipophilic epoxide were combined, worked up, and the product crystallised from methanol to yield 50 mg of the epoxide *IX*, 105–107°C, $[\alpha]_D^{20}$ +23° (*c* 1·38). ^{1}H-NMR: 0·34 (d of doublets, $J_{gem} = 4·5$ Hz, $J_{vic} = 9$ Hz, one cyclopropane proton), 0·65 (s, 18-H), 0·70 (t, $J_{gem} = J_{vic} = 4·5$ Hz, one cyclopropane proton), 0·82 (s, 19-H), 0·86 (d, $J = 6·5$ Hz, 0·91 (d, $J = 6$ Hz, 21-H), 1·97 (d of doublets, $J_{1,1} = 15$ Hz, $J_{1\beta,2} = 3$ Hz, 1β-H), 3·05 (broad t, 2-H), 3·37 (t, $J_{2,3} = J_{3,4} = 4$ Hz, 3-H). For $C_{27}H_{44}O$ (384·6) calculated: 84·31% C, 11·53% H; found: 84·21% C, 11·40% H.

2α,3α-Epoxy-4α,5-cyclo-A-homo-B-nor-5α-cholestane (*X*)

Fractions with the polar epoxide from the foregoing experiment were combined, solvent removed, and the residue was crystallised from methanol to yield 78 mg of the epoxide *X*, m.p. 110–112°C,

$[\alpha]_D^{20}$ +25° (*c* 1·27). ^{1}H-NMR: 0·41 (t, $J_{gem} = J_{vic} = 5$ Hz, one cyclopropane proton), 0·61 (d of doublets, one cyclopropane proton), 0·64 (s, 18-H), 0·73 (s, 19-H), 0·845 (d, $J = 6$ Hz, 26-H and 27-H), 0·90 (d, $J = 6$ Hz, 21-H), 2·99 (q, $J_{2,1\alpha} = J_{2,1\beta} = 4$ Hz, $J_{2,3} = 4$ Hz, 2β-H), 3·18 (d of doublets $J_{2,3} = 4$ Hz, $J_{3,4} = 1$ Hz, 3β-H). For $C_{27}H_{44}O$ (384·6) calculated: 84·31% C, 11·53% H; found: 84·21% C, 11·40% H.

4α,5-Cyclo-A-homo-B-nor-5α-cholestan-2β-ol (*XI*)

a) *From* 4α,5-*cyclo*-A-*homo*-B-*nor*-5α-*cholestan*-2-*one* (VII): The ketone *VII* (150 mg) in tetrahydrofuran (4 ml) was treated with lithium tri-tert-butoxyaluminium hydride (300 mg) and allowed to stand at room temperature for 30 minutes. The excess reducing agent was removed with 5% acetic acid, the mixture was diluted with ether and water, and acidified with hydrochloric acid. The ethereal layer was worked up, and the residue was crystallised from methanol to yield 60 mg of the alcohol *XI*, m.p. 117–118°C, $[\alpha]_D^{20}$ +2° (1·16). IR: 3055 (cyclopropane), 3625, 1037, 1027 cm^{-1} (hydroxyl). ^{1}H-NMR: 0·29 and 0·70 (broad s and mt, two cyclopropane protons), 0·865 (d, $J = 6$ Hz, 26-H and 27-H) 0·88 (s, 19-H), 0·67 (s, 18-H), 0·925 (d, $J = 6$ Hz, 21-H), 3·74 (broad mt, $W = 31$ Hz, 2α-H axial). For $C_{27}H_{46}O$ (386·6) calculated: 83·87% C, 11·99% H; found: 84·01% C, 12·04% H.

b) *From* 2β,3β-*epoxy*-4α,5-*cyclo*-A-*homo*-B-*nor*-5α-*cholestane* (IX): The epoxide *IX* (150 mg) in tetrahydrofuran (40 ml) was treated with lithium aluminium hydride (300 mg) and refluxed for 5 h. The mixture was diluted with wet ether, the excess hydride was decomposed with ethyl acetate, and the mixture was acidified with hydrochloric acid. The ethereal solution was worked up and solvent removed. The product was chromatographed on a silica gel column (15 g) in benzene–ether (49 : 1). Fractions with the lipophilic component were combined, solvent removed, and the residue was crystallised from methanol to yield 85 mg of the alcohol *XI*, m.p. 117–119°C, $[\alpha]_D^{20}$ +1° (*c* 1·18), identical with the compound prepared as under *a*).

2β-Methanesulphonyloxy-4α,5-cyclo-A-homo-B-nor-5α-cholestane (*XII*)

The alcohol *XI* (40 mg) in pyridine (0·8 ml) was treated at 0°C with methanesulphonyl chloride (0·1 ml) and allowed to stand at the same temperature for 1 h. The mixture was decomposed with ice, the product taken into ether, and the ethereal solution was worked up. The residue was crystallised from ether–methanol to yield 25 mg of the mesylate *XII*, m.p. 101–102°C, $[\alpha]_D^{20}$ 0° (*c* 0·97). IR: 3055 (cyclopropane), 1366, 1343, 1178, 944, 919 cm^{-1} (mesylate). For $C_{28}H_{48}O_3S$ (464·7) calculated: 72·36% C, 10·41% H, 6·90% S; found: 72·12% C, 10·30% H, 7·19% S.

4α,5-Cyclo-A-homo-B-nor-5α-cholestan-3β-ol (*XIII*)

Elution of the chromatography after isolation of the 2β-hydroxy derivative *XI* under *b*) with the same solvent mixture afforded fractions with the polar component. Working up and crystallisation from methanol gave 28 mg of the alcohol *XIII*, m.p. 122–123°C, identical with the authentic sample[1].

4α,5-Cyclo-A-homo-B-nor-5α-cholestan-2α-ol (*XIV*)

The epoxide *X* (150 mg) in tetrahydrofuran (30 ml) was treated with lithium aluminium hydride (300 mg) and refluxed for 5 h. The mixture was worked up as described for the 2β-epimer *XI* under *a*). The product was chromatographed on a silica gel column (20 g) in benzene. Fractions

with the polar component were combined, solvent removed, and the product crystallised from methanol to yield 40 mg of the alcohol *XIV*, m.p. 122–123°C, $[\alpha]_D^{20}$ +12° (*c* 1·23). IR: 3060 (cyclopropane), 3625, 1032 cm^{-1} (hydroxyl). ^{1}H-NMR: 0·69 (s, 18-H), 0·835 (s, 19-H), 0·87 (d, J = 6·5 Hz, 26-H and 27-H), 0·94 (d, J = 6 Hz, 21-H), 3·46 (broad mt, W = 30 Hz, 2β-H_{axial}). For $C_{27}H_{46}O$ (386·6) calculated: 83·87% C, 11·99% H; found: 83·70% C, 11·81% H.

4α,5-Cyclo-A-homo-B-nor-5α-cholestan-3α-ol (*XV*)

Fractions with the lipophilic component from the chromatography of the foregoing experiment were worked up to yield after evaporation of the solvent 63 mg of the oily alcohol *XV*, identical with the authentic sample.[1]

4α,5-Cyclo-A-homo-B-nor-5α-cholest-1-en-3-one (*XVI*)

a) *From* 2α-*bromo*-4α,5-*cyclo*-A-*homo*-B-*nor*-5α-*cholestan*-3-*one* (III): The bromo ketone *III* (400 mg) in *sym*-collidine (12 ml) was heated to 160°C for 20 h. Collidine was removed under reduced pressure, the residue was dissolved in ether, and the ethereal solution worked up. The crystalline product was chromatographed on a silica gel column (25 g) in benzene to yield after crystallisation from methanol 150 mg of the unsaturated ketone *XVI*, m.p. 71–73°C, $[\alpha]_D^{20}$ +189° (*c* 1·25). IR: 3060, 3030 (cyclopropane and double bond), 1665, 1600 cm^{-1} (carbonyl). ^{1}H-NMR: 0·71 (s, 18-H), 0·865 (d, J = 6 Hz, 26-H and 27-H), 0·925 (d, J = 6 Hz, 21-H), 1·035 (s, 19-H), 5·76 (d of doublets, $J_{2,1}$ = 10 Hz, $J_{2,4}$ = 1 Hz, 2-H), 6·445 (d, $J_{1,2}$ = 10 Hz, 1-H). For $C_{27}H_{42}O$ (382·6) calculated: 84·75% C, 11·07% H; found: 85·01% C, 11·30% H.

b) *From* 4α,5-*cyclo*-A-*homo*-B-*nor*-5α-*cholest*-1-*en*-3α-*ol* (XVII): The alcohol *XVII* (85 mg) in acetone (2 ml) was treated with excess Jones' reagent and allowed to stand at room temperature for 10 minutes. The excess reagent was removed with methanol, the mixture was diluted with water, and the product taken into ether. The ethereal solution was worked up, and the product was chromatographed on a silica gel column (15 g) in benzene–ether (3 : 1). Working up of the corresponding fractions and crystallisation from methanol afforded 25 mg of the ketone *XVI*, m.p. 71–73°C, $[\alpha]_D^{20}$ +186° (*c* 1·84), identical with the sample prepared as under *a*).

c) *From* 4α,5-*cyclo*-A-*homo*-B-*nor*-5α-*cholest*-1-*en*-3β-*ol* (XVIII): The alcohol *XVIII* (100 mg) in acetone (2 ml) was oxidised with Jones' reagent as described in the foregoing experiment. Similar working up, chromatography, and crystallisation from methanol gave 32 mg of the ketone *XVI*, m.p. 71–73°C, $[\alpha]_D^{20}$ +187° (*c* 1·32), identical with the sample prepared as under *a*).

4α,5-Cyclo-A-homo-B-nor-5α-cholest-1-en-3α-ol (*XVII*)

The ketone *XVI* (2·5 g) in ethyl acetate (35 ml) and methanol (100 ml) was treated with sodium borohydride (600 mg) and the mixture was stirred at room temperature for 8 h. The excess hydride was removed with acetic acid, solvents distilled off under reduced pressure, the residue was diluted with water, and the product extracted into ether. The ethereal solution was worked up, and the residue after evaporation of the solvent was chromatographed on a silica gel column in benzene. Fractions with the lipophilic component were combined, solvent removed, and the product was crystallised from acetone–water to yield 210 mg of the alcohol *XVII*, m.p. 104 to 106°C. $[\alpha]_D^{20}$ −20° (*c* 1·34). Mass spectrum: M^+ 384. IR: 3060, 3025 (cyclopropane), 3610, 1019, 1000, 980 (hydroxyl), 1658 cm^{-1} (double bond). ^{1}H-NMR: 0·17 and 0·61 (t and two d, cyclopropane protons), 0·69 (s, 18-H), 0·87 (d, J = 6·5 Hz, 26-H and 27-H), 0·865 (s, 19-H), 0·925 (d, J = 6·5 Hz, 21-H), 4·245 (d, $J_{3,2}$ = 2·7 Hz, 3-H), 5·54 (ν_A = 5·569, ν_B = 5·510, J_{AB} =

= 10·4 Hz, 1-H and 2-H). For $C_{27}H_{44}O$ (384·6) calculated: 84·31% C, 11·53% H; found: 84·12% C, 11·21% H.

4α,5-Cyclo-A-homo-B-nor-5α-cholest-1-en-3β-ol (*XVIII*)

Elution of the chromatography of the foregoing experiment with the same solvent afforded fractions containing the polar component. Working up and crystallisation from acetone–water gave 1·2 g of the alcohol *XVIII*, m.p. 86–87°C, $[\alpha]_D^{20}$ +23·1° (*c* 1·25). IR: 3065, 3025 (cyclopropane), 3610, 1019, 1000, 980 (hydroxyl), 1658 cm^{-1} (double bond). ^{1}H-NMR: 0·33 and 0·59 (t and mt, cyclopropane protons), 0·68 (s, 18-H), 0·86 (d, J = 6·5 Hz, 26-H and 27-H), 0·87 (s, 19-H), 0·91 (d, J = 6·5 Hz, 21-H), 4·51 (d, $J_{3,4}$ = 7 Hz, 3-H), 5·42 (ν_A = 5·454, ν_B = 5·386, $J_{A,B}$ = 10·8 Hz). For $C_{27}H_{44}O$ (384·6) calculated: 84·31% C, 11·51% H; found: 84·02% C, 11·31% H.

The analyses were carried out in the Analytical Laboratory of this Institute by Mr V. Štěrba and Mrs E. Sýkorová under the direction of Dr J. Horáček. The infra red spectra were recorded by Mr P. Formánek under the direction of Dr J. Smoliková. The ^{1}H-NMR *spectra were recorded and interpreted by Dr M. Buděšínský. The mass spectra were recorded and interpreted by Dr A. Trka.*

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