SYNTHESIS OF 6β,7aβ-CYCLO-B-HOMO-5α-CHOLEST-2-ENE*

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Synthesis of 6β,7aβ-cyclo-B-homo-5α-cholest-2-ene from 3β-acetoxy-5α-cholestan-7-one is described.

In connection with our studies of cyclo-B-homosteroids 6β,7aβ-cyclo-B-homo-5α--cholest-2-ene (*XIII*) became of interest as the starting material for synthesis of cyclosteroids substituted in ring A. In this paper we describe synthesis of this compound.

The olefin *V* represented the key-intermediate in the adopted reaction sequence. It was prepared in three steps from the ketone *I* as follows: Bromination with bromine in chloroform afforded a mixture of the bromo ketones *II* epimeric at $C_{(6)}$. It was reduced in crude state with sodium borohydride in ethanol to yield the bromohydrins *III* and *IV*. They were separated by column chromatography and the structures were assigned on the basis of the ^{1}H-NMR evidence. Both bromohydrins afforded the olefin *V* on reaction with zinc in acetic acid.

Simmons–Smith methylenation of the 6,7-double bond yielded 3β-acetoxy-6β,7aβ--cyclo-B-homo-5α-cholestane (*VII*) as the sole product. The configuration of the cyclopropane ring follows from the ^{1}H-NMR data: It is well known from the literature[1–3] that the cyclopropane ring exhibits a deshielding effect on the 19-protons if those protons are lying outside of the conical region extending above and below the plane of cyclopropane ring. Those lying in these conical regions are shielded. Fig. 1 shows models of our 6,7a-cyclo-derivatives. 19-Protons of the 6α,7aα-epimer are evidently lying in the conical region, and we would expect a strong shielding. 19-Protons of the 6β,7aβ-epimer are lying on the border of the conical region (the angle believed to be about 110°) (ref.[4]) which should produce only a weak – shielding or deshielding – effect. In our compound the signal of the 19-protons lies at 0·84 p.p.m. like in the parent 3β-acetoxy-5α-cholestane (0·84 p.p.m.) (ref.[5]). It is therefore the 6β, 7aβ-isomer *VII*.

Hydrolysis of the acetoxy group gave the alcohol *VI* which was oxidised to the ketone *IX*. Metal hydride reduction afforded a mixture of the epimeric alcohols *VI* and *X*

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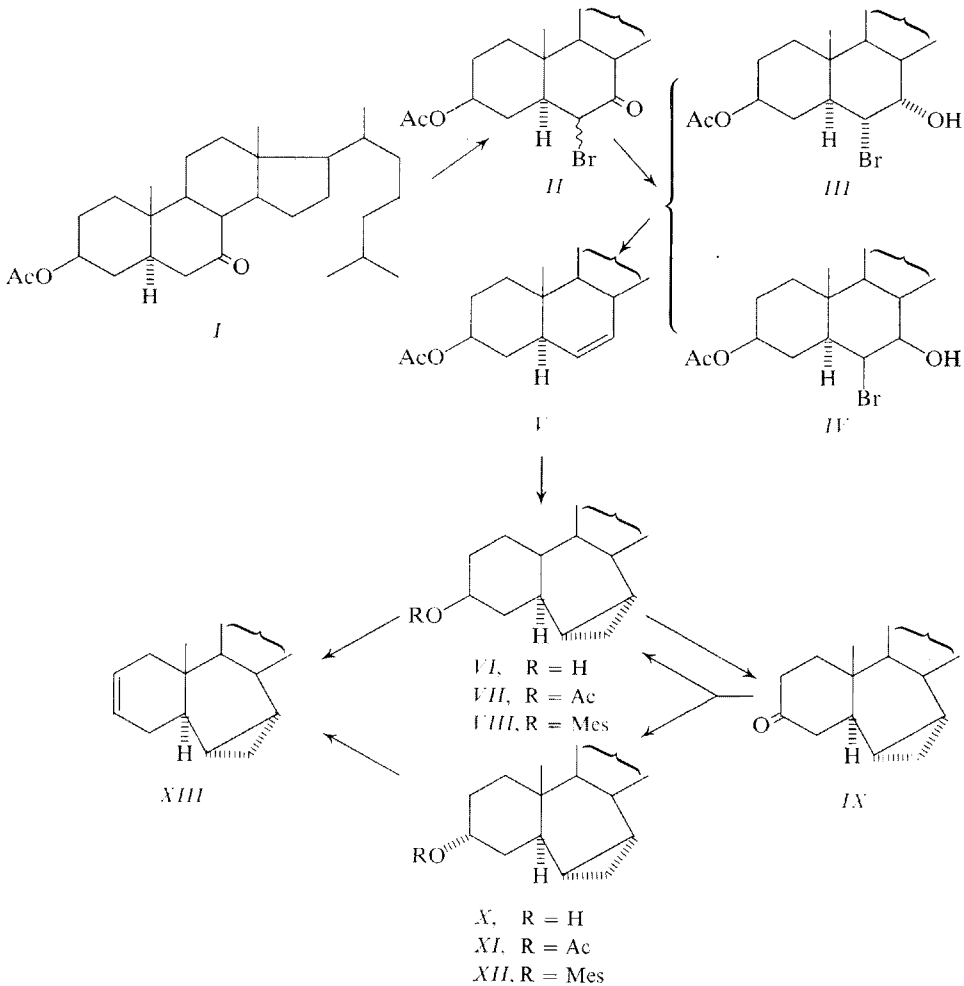
the proportions being dependent on the nature of the hydride used. Maximum of the 5α-epimer *X* (20%) was obtained with sodium borohydride in methanol.

The alcohols *VI* and *X* were transformed to the mesylates *VIII* and *XII* with methanesulphonyl chloride in pyridine. Both mesylates afforded on reflux with *sym*-collidine the desired olefin *XIII*. The same olefin was also obtained as the main product on acetolyses of the mesylates (acetic acid–sodium acetate) next to the epimeric acetates *VII* and *XI*.



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 20 spectrometer in tetrachloromethane unless otherwise stated.

The ^{1}H-NMR spectra were recorded on the Tesla 80-MHz instrument (compound *VII* and *XIII* on Varian 60-MHz instrument) in deuteriochloroform and corrected to tetramethylsilane (7·25 p.p.m.) unless otherwise stated. The chemical shifts is given in p.p.m. The mass spectra were recorded on the mass spectrometer AEI MS 902. The identity of samples prepared by different routes was checked by mixture melting point determination, by thin-layer chromatography (TLC), and by infrared spectra. PLC = preparative-layer chromatography. Ligroin of b.p. 40—60°C was used as solvent. Usual working up of an ethereal solution means extraction with 5% hydrochloric acid, water, 5% sodium hydrogen carbonate, water, drying with sodium sulphate, and evaporation of the solvent.

3β-Acetoxy-6α-bromo-5α-cholestan-7α-ol (*III*)

A solution of the ketone *I* (38 g) in chloroform (250 ml) was treated dropwise in the course of 15 minutes with bromine (14·8 g) in chloroform (300 ml). After 30 minutes at room temperature the mixture was poured in water, and extracted with ether. The ethereal extract was washed with 10% sodium thiosulphate, water, sodium hydrogen carbonate, water, dried, and the solvent was removed under reduced pressure to yield 45 g of mixture of at $C_{(6)}$ epimeric bromo ketones (*II*). The mixture showed one spot on TLC. It was dissolved in methanol (4000 ml) treated with sodium borohydride (80 g) and allowed to stand at room temperature for 2 hours. The excess hydride was then decomposed with ice and 5% hydrochloric acid. The volume of the reaction mixture was evaporated under reduced pressure to about 800 ml, the residue was diluted with water, and the product extracted into ether. The ethereal solution was worked up to yield 44 g of an oil which was chromatographed over silica gel (1 kg) in ligroin–ether (49 : 1). Fractions containing the lipophilic bromohydrin were combined, the solvent removed, and the residue was crystallised from methanol to yield 20 g of the bromohydrin *III*, m.p. 107—110°C, $[\alpha]_D^{20}$ +30° (*c* 1·95). IR: 3580 (hydroxyl-bonded), 1739, 1245, 1030 cm^{-1} (acetate). ^{1}H-NMR: 0·65 (s,18-H),

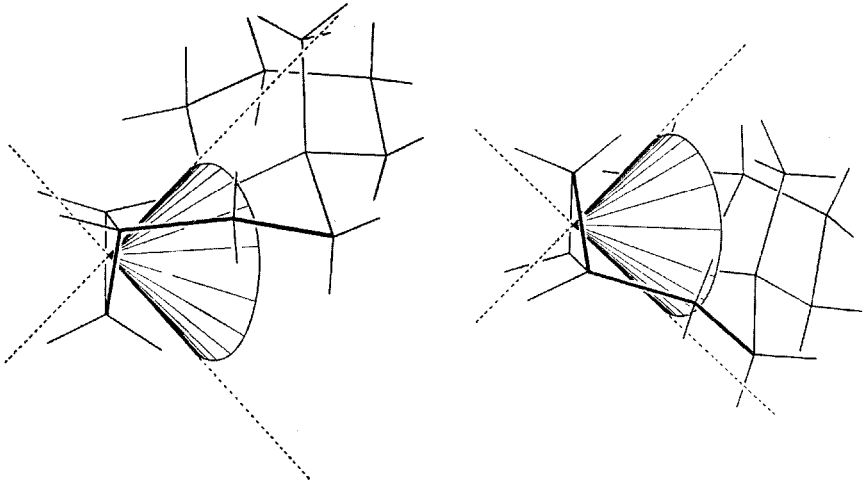


FIG. 1

Shielding/Deshielding of 19-Protons in the Epimeric 6,7a-Derivatives

0·86 (d, $J = 6$ Hz, 26- and 27-H),0·89 (s, 19-H), 0·90 (d, $J = 5·5$ Hz, 21-H), 2·025 (s, acetate), 3·89 (unresolved mt, $W = 5$ Hz, 7β-H), 4·24 (dd, $J_{6,7} = 2·5$ Hz, $J_{5,6} = 11·5$ Hz, 6β-H), 4·68 (broad mt, 3α-H). For $C_{29}H_{49}BrO_3$ (525·6) calculated: 66·27% C, 9·40% H, 15·20% Br; found: 66·35% C, 9·41% H, 15·08% Br.

3β-Acetoxy-6β-bromo-5α-cholestan-7β-ol (*IV*)

Elution of the chromatography of the foregoing experiment with the same solvent mixture afforded fractions with the polar component. The residue (15·5 g) obtained after working up was crystallised from methanol to yield 11 g of the bromohydrin *IV*, m.p. 80°C (decomp), $[\alpha]_D^{20}$ +10° (*c* 1·02). IR: 3565 (hydroxyl bonded), 1739, 1243, 1030 cm^{-1} (acetate). ^{1}H-NMR: 0·70 (s, 18-H), 0·875 (d, $J = 6$ Hz, 26- and 27-H), 0·90 (d, $J = 5·5$ Hz, 21-H), 1·10 (s, 19-H), 2·01 (s, acetate), 2·30 (unressolved mt, probably 8α-H), 3·19 (dd, $J_{7,6} = 4$ Hz, $J_{7,8} = 9·5$ Hz, 7α-H), 4·45 (mt, $W = 7$ Hz, 6α-H), 4·76 (broad mt, 3α-H). For $C_{29}H_{49}BrO_3$ (525·6) calculated: 66·27% C, 9·40% H, 15·20% Br; found: 66·19% C, 9·46% H, 15·45% Br.

3β-Acetoxy-5α-cholest-6-ene (*V*)

a) *From* 3β-*acetoxy*-6α-*bromo*-5α-*cholestan*-7α-*ol*(III): The bromohydrin *III* (1 g) in acetic acid (30 ml) was refluxed with zinc powder (2 g) for 4 hours. The solids were filtered off, the filtrate was diluted with water, and the product taken into ether. The extract was washed with water, with saturated potassium hydrogen carbonate solution, water, dried, and the solvent was removed. The residue (532 mg) was crystallised from methanol to yield 370 mg of the olefin *V*, m.p. 108 to 110°C, $[\alpha]_D^{20}$ −88° (*c* 1·23) in accordance with the literature[6].

b) *From* 3β-*acetoxy*-6β-*bromo*-5α-*cholestan*-7β-*ol* (IV): The bromohydrin *IV* (1 g) was treated similarly as described in the foregoing experiment. Working up and crystallisation from methanol yielded 320 mg of the olefin *V*, m.p. 107—110°C.

3β-Acetoxy-6β,7aβ-cyclo-B-homo-5α-cholestane (*VII*)

a) *From* 3β-*acetoxy*-5α-*cholest*-6-*ene* (V): 0·7% Zn—Cu couple was prepared by adding zinc dust (5·2 g) into a solution of cupric acetate monohydrate (120 mg) in acetic acid (10 ml) at 50—60°C and shaking until the solution decolorised. Sedimented zinc was decanted with eight portions of ether (10 ml each). The couple was transfered to an autoclave, a solution of the olefin *V* (1·5 g) in absol. ether (25 ml) and diiodomethane (4·6 ml) were added, and heated to 100°C for 6 hours. After cooling off to room temperature the remaining metal was decanted with ether and the solution was poured into 5% potassium hydrogen carbonate. The ethereal layer was washed with water, potassium hydrogen carbonate solution, 5% hydrochloric acid, 5% potassium hydrogen carbonate solution, water, 10% sodium thiosulphate solution, water, dried, and evaporated. The residue was chromatographed over silica gel (20 g), in ether–ligroin (1 : 99). Fractions containing the starting olefin *V* and the desired product (identical polarity on TLC) were combined and evaporated to yield 1·35 g of an oil. It was dissolved in ether (20 ml) and treated with a solution of perphthalic acid (1·35 g) in 13·5 ml of ether. After standing overnight at room temperature the excess peracid was removed with a potassium hydrogen carbonate solution. The ethereal layer was washed with water, dried and ether distilled off. The residue was chromatographed on a silica gel column (40 g) in ether–ligroin (1 : 99). Fractions containing the lipophilic component were combined, evaporated, and the residue (769 mg) was crystallised from methanol to yield 465 mg of the acetate *VII*, m.p. 99—101°C, $[\alpha]_D^{20}$ −40° (*c* 2·72). IR: 3065 (cyclopropane), 1735, 1245, 1030 cm^{-1} (acetate). Mass spectrum: M^+ 442. ^{1}H-NMR: −0·05

and +0·45 (two mt, two cyclopropane protons), 0·72 (s, 18-H), 0·84 (s, 19-H), 0·89 (d, $J = 6$ Hz, 26- and 27-H), 0·91 (d, $J = 6$ Hz, 21-H), 2·04 (s, acetate), 4·7 (broad mt, 3α-H). For $C_{30}H_{50}O_2$ (442·7) calculated: 81·39% C, 11·38% H; found: 81·39% C, 11·34% H.

b) *From* 3β-*methanesulphonyloxy*-6β,7aβ-*cyclo*-B-*homo*-5α-*cholestane* (VIII): Elution of the chromatography after preparation of the olefin *XIII* under *a*) afforded fractions containing the more polar acetate. Working up and crystallisation from ethanol yielded 113 mg of the acetate *VII*, m.p. 99—100°C, $[\alpha]_D^{20}$ −38° (*c* 1·19).

c) *From* 3α-*methanesulphonyloxy*-6β,7aβ-*cyclo*-B-*homo*-5α-*cholestane* (XII): Elution of the chromatography after preparation of the olefin *XIII* under *b*) afforded fractions with the more polar acetate. Working up and crystallisation from ethanol yielded 22 mg of the acetate *VII*, m.p 99—100°C, $[\alpha]_D^{20}$ −38° (*c* 1·26).

6β,7aβ-CycIo-B-homo-5αcholestan-3β-ol (*VI*)

a) *From* 3β-*acetoxy*-6β,7aβ-*cyclo*-B-*homo*-5α-*cholestane* (VII): The acetate *VII* (180 mg) in methanol (20 ml) was treated with a solution of potassium hydroxide (300 mg) in methanol (10 ml) and allowed to stand at room temperature for 2 hours. The solvent was removed under reduced pressure the residue was treated with water, and the product extracted with ether. The ethereal solution was washed with water, dried, and the solvent distilled off. The residue was crystallised from methanol–water to give 85 mg of the alcohol *VI*, m.p. 53—56°C, $[\alpha]_D^{20}$ −47° (*c* 1·09). IR: 3065 (cyclopropane), 3625, 1042 cm^{-1} (hydroxyl). ^{1}H-NMR: −0·09 and +0·42 (broad mts, two cyclopropane protons), 0·725 (s, 18-H), 0·84 (s, 19-H), 0·875 (d, $J = 6{,}5$ Hz, 26- and 27-H), 0·925 (d, $J = 6$ Hz, 21-H), 1·55 (s, hydroxyl), 3·53 (broad mt, 3α-H). For $C_{28}H_{48}O$ (400·7) calculated: 83·93% C, 12·08% H; found: 84·00% C, 12·00% H.

b) *From* 6β,7aβ-*cyclo*-B-*homo*-5α-*cholestan*-3-*one* (IX) *with lithium tri-tert-butoxyaluminium hydride*: A solution of the ketone *IX* (230 mg) in tetrahydrofuran (30 ml) was treated with solid lithium tri-tert-butoxyaluminium hydride (460 mg) and allowed to stand at room temperature for 30 minutes. The excess hydride was removed with dilute hydrochloric acid and water, the product was taken into ether, and the ethereal solution was worked up. The residual oily product (220 mg) was purified by PLC (ligroin–ether 2 : 1) to yield 200 mg of a crystalline product. Crystallisation from methanol afforded 111 mg of the alcohol *VI*, m.p. 53—55°C, $[\alpha]_D^{20}$ −40° (*c* 0·56).

c) *From the ketone* IX *with lithiumaluminium hydride*: Elution of the chromatography after preparation of the alcohol *X* under *a*) afforded 240 mg of the polar component. Crystallisation from methanol gave 210 mg of the alcohol *VI*, m.p. 52—55°C, $[\alpha]_D^{20}$ −46° (*c* 1·12).

d) *From the ketone* IX *with sodium borohydride*: Elution of the chromatography after preparation of the alcohol *X* under *b*) afforded 2·42 g of the polar component. Crystallisation from methanol afforded 1·65 g of the alcohol *VI*, m.p. 52—55°C, $[\alpha]_D^{20}$ −43° (*c* 1·32).

e) *From the ketone* IX *with lithium borohydride*: The crude product obtained on preparation of the alcohol *X* under *c*) was purified by PLC. The zones with the polar component were collected, the product eluted with ether, and solvent removed. Crystallisation from methanol yielded 306 mg of the alcohol *VI*, m.p. 52—55°C, $[\alpha]_D^{20}$ −41° (*c* 1·32).

3β-Methanesulphonyloxy-6β,7aβ-cyclo-B-homo-5α-cholestane (*VIII*)

A solution of the alcohol *VI* (400 mg) in pyridine (8 ml) was treated at +5°C with methanesulphonyl chloride (0·6 ml) and set aside at room temperature for 4 hours. The reaction mixture

was decomposed with ice and water, the product taken into ether, and the ethereal solution was worked up in the usual way. The residue (430 mg) was crystallised from n-heptane to yield 270 mg of the mesylate *VIII*, m.p. 95–97°C, $[\alpha]_D^{20}$ −39° (*c* 1·48). IR: 3065 (cyclopropane), 1366, 1344, 1177 cm^{-1} (mesylate). ^{1}H-NMR: −0·04 and +0·53 (two mts, two cyclopropane protons), 0·75 (s, 18-H), 0·88 (s, 19-H), 0·91 (d, J = 6 Hz, 26- and 27-H), 0·94 (d, J = 6 Hz, 21-H), 3·04 (s, mesylate), 4·58 (mt, 3α-H). For $C_{30}H_{50}O_3S$ (490·7) calculated: 73·43% C, 10·27% H, 6·52% S; found: 73·61% C, 10·48% H, 6·75% S.

6β,7aβ-Cyclo-B-homo-5α-cholestan-3-one (*IX*)

a) *From* 6β,7aβ-*cyclo*-B-*homo*-5α-*cholestan*-3β-*ol* (VI): A solution of the alcohol *VI* (90 mg) in acetone (10 ml) was treated with excess Jones' reagent and allowed to stand at room temperature for 5 minutes. The excess oxidising agent was removed with methanol (1 ml) and after 5minutes at room temperature the mixture was diluted with water, the product was taken into ether, the ethereal solution was washed with sodium hydrogen carbonate, water, dried, and the solvent was removed. The residue (74 mg) was crystallised from methanol–ethanol to yield 46 mg of the ketone *IX*, m.p. 106–108°C, $[\alpha]_D^{20}$ +3° (*c* 0·38). IR: 3065 (cyclopropane), 1714 cm^{-1} (ketone). ^{1}H-NMR (in C_6D_6): 0·305 (mt, one cyclopropane proton), 0·83 (s, 18-H), 0·83 (s, 19-H), 1·055 (d, J = 6 Hz, 26- and 27-H), 1·135 (d, J = 6 Hz, 21-H). For $C_{28}H_{46}O$ (398·7) calculated: 84·35% C, 11·63% H; found: 84·18% C, 11·48% H.

b) *From* 6β,7aβ-*cyclo*-B-*homo*-5α-*cholestan*-3α-*ol* (X): The alcohol *X* (25 mg) in acetone (2 ml) was oxidised with Jones' reagent as described in the previous experiment. Working up and crystallisation from methanol yielded 17 mg of the ketone *IX*, m.p. 107–109°C, $[\alpha]_D^{20}$ +3° (*c* 0·13).

6β,7aβ-Cyclo-B-homo-5α-cholestan-3α-ol (*X*)

a) *With lithium aluminiumhydride*: Lithium aluminiumhydride (1·5 g) was added to a solution of the ketone *IX* (300 mg) in tetrahydrofuran (100 ml). After 2 hours at room temperature the excess hydride was decomposed with ethyl acetate and the product extracted with ether. The ethereal layer was worked up to leave 300 mg of an oily residue consisting of two products (TLC). It was chromatographed over silica gel (50 g) in ligroin–ether (19 : 1). Fractions with the lipophilic component were combined, the solvent was removed and the residue crystallised from acetone to yield 26 mg of the alcohol *X*, m.p. 88–90°C, $[\alpha]_D^{20}$ −36° (*c* 1·87). IR: 3065 (cyclopropane), 3628, 1021, 1005 cm^{-1} (hydroxyl). ^{1}H-NMR: −0·13 to +0·56 (mts, two cyclopropane protons), 0·73 (s, 18-H), 0·80 (s, 19-H), 0·89 (d, J = 6·5 Hz, 26- and 27-H), 0·91 (d, J = 6 Hz, 21-H), 4.05 (mt, W = 12 Hz, 3β-H). For $C_{28}H_{48}O$ (400·7) calculated: 83·93% C, 12·08% H; found: 83·71% C, 11·91% H.

b) *With sodium borohydride*: A solution of the ketone *IX* (3·85 g) in ethanol (385 ml) was treated with sodium borohydride (4 g). After two hours at room temperature the excess hydride was removed with water and 1% hydrochloric acid, the mixture was diluted with water, and the product taken into ether. The ethereal layer was worked up to yield 3·5 g of a mixture which was chromatographed on a silica gel column (150 g) in ligroin–ether (19 : 1). Fractions with the lipophilic alcohol afforded 721 mg of the product which was crystallised from acetone to give 420 mg of the alcohol *X*, m.p. 88–90°C, $[\alpha]_D^{20}$ −37° (1·18).

c) *With lithium borohydride*: A solution of the ketone *IX* (380 mg) in tetrahydrofuran (20 ml) was treated with lithium borohydride (800 mg) and refluxed for 2 hours. The excess hydride was decomposed with methanol, water, and 5% hydrochloric acid. The product was extracted into ether, the ethereal solution was worked up in the usual way, and the residue was chromatographed

on 6 plates of silica gel (20 × 20 cm) in ligroin–ether (2 : 1). The zones with the lipophilic component were worked up and the product crystallised from acetone to yield 36 mg of the alcohol *X*, m.p. 88–90°C, $[\alpha]_D^{20}$ −40° (*c* 1·24).

3α-Acetoxy-6β,7aβ-cyclo-B-homo-5α-cholestane (*XI*)

a) *From* 6β,7aβ-*cyclo*-B-*homo*-5α-*cholestan*-3α-*ol* (X): The alcohol *X* (300 mg) in pyridine (2 ml) was treated with acetic anhydride (1·2 ml) and allowed to stand overnight at room temperature. The mixture was decomposed with ice, the product taken into ether, and the ethereal solution was worked up in the usual way. The residue after evaporation of the solvent (340 mg) was crystallised from methanol to yield 70 mg of the acetate *XI*, m.p. 99–100°C, $[\alpha]_D^{20}$ −27° (*c* 0·45). IR: 3065 (cyclopropane), 1735, 1255, 1235, 1021 cm^{-1} (acetate). ^{1}H-NMR: −0·025 and 0·425 (mts, three cyclopropane protons), 0·735 (s, 18-H), 0·82 (s, 19-H). 0·895 (d, J = 6 Hz, 26- and 27-H), 0·92 (d, J = 6 Hz, 21-H), 2·07 (s, 3α-acetate), 5·05 (mt, 3β-H). For $C_{30}H_{50}O_2$ (442·7) calculated: 81·39% C, 11·38% H; found: 81·82% C, 11·62% H.

b) *From* 3β-*methanesulphonyloxy*-6β,7aβ-*cyclo*-B-*homo*-5α-*cholestane* (VIII): Elution of the chromatography after preparation of the olefin *XIII* according to *a*) with the same solvent mixture afforded fractions with the less polar acetate. Working up and crystallisation from methanol gave 5 mg of the acetate *XI*, m.p. 96–99°C, $[\alpha]_D^{20}$ −25° (*c* 0·45).

c) *From* 3α-*methanesulphonyloxy*-6β,7aβ-*cyclo*-B-*homo*-5α-*cholestane* (XII): Elution of the chromatography after preparation of the olefin *XIII* according to *b*) yielded fractions with the less polar acetate. Working up and crystallisation from methanol gave 3·2 mg of the acetate *XI*, m.p. 96–98°C, $[\alpha]_D^{20}$ −21° (*c* 0·37).

3α-Methanesulphonyloxy-6β,7aβ-cyclo-B-homo-5α-cholestane (*XII*)

A solution of the alcohol *X* (290 mg) in pyridine (6 ml) was treated at +5°C with methanesulphonyl chloride (0·6 ml) and allowed to stand at room temperature for 4 hours. The reaction mixture was decomposed with ice, the product was taken into ether, and the ethereal solution was worked up. The residue was crystallised from n-heptane to yield 195 mg of the mesylate *XII*, m.p. 102–103°C, $[\alpha]_D^{20}$ −34° (*c* 1·96). IR: 3065 (cyclopropane), 1365, 1341, 1181, 1160, 907 cm^{-1} (mesylate). ^{1}H-NMR: 0·01 and 0·46 (two mts, two cyclopropane protons), 0·71 (s, 18-H), 0·80 (s, 19-H), 0·88 (d, J = 6 Hz, 26- and 27-H), 0·89 (d, J = 6 Hz, 21-H), 3·00 (s, mesylate), 4·98 (mt, 3β-H). For $C_{30}H_{50}O_3S$ (490·7) calculated: 73·43% C, 10·27% H, 6·52% S; found: 74·01% C, 10·58% H, 6·97% S.

6β,7aβ-Cyclo-B-homo-5α-cholest-2-ene (*XIII*)

a) *From* 3β-*methanesulphonyloxy*-6β,7aβ-*cyclo*-B-*homo*-5α-*cholestane* (VIII) *under conditions of acetolysis*: The mesylate *VIII* (400 mg) in acetic acid (10 ml) was treated with acetic anhydride (1 ml) and anhydrous sodium acetate (400 mg) and refluxed for 5 hours. The mixture was poured into water, the product extracted with ether, and the ethereal solution was washed with water, saturated potassium hydrogen carbonate solution, water, dried, and the solvent removed. The oily residue (360 mg) was chromatographed over silica gel (40 g) in ligroin–ether (19 : 1). Fractions with the lipophilic olefin were combined, the solvent removed, and the residue was crystallised from ethanol to yield 204 mg of the olefin *XIII*, m.p. 69–71°C, $[\alpha]_D^{20}$ +5° (*c* 1·28). IR (CS_2): 3065, 3025, 1652, 1626, 667 cm^{-1}. ^{1}H-NMR: −0·05 and +0·44 (two mts, three cyclopropane protons), 0·73 (s, 18-H), 0·76 (s, 19-H), 0·87 (d, J = 6 Hz, 26- and 27-H), 0·92 (d, J = 6 Hz,

21-H), 5·54 (mt, olefinic protons). For $C_{28}H_{46}$ (382·7) calculated: 87·88% C, 12·12% H; found: 87·55% C, 12·19% H.

b) *From* 3α-*methanesulphonyloxy*-6β,7aβ-*cyclo*-B-*homo*-5α-*cholestane* (XII): *The mesylate XII* (270 mg) in acetic acid (5·4 ml) and acetic anhydride (0·54 ml) was refluxed with anhydrous sodium acetate (270 mg) for 5 hours. The mixture was worked up as described in the previous experiment to yield 220 mg of an oily product which was chromatographed on a silica gel column (40 g) in ligroin–ether (33 : 1). The corresponding fractions afforded after working up and crystallisation from ethanol 120 mg of the olefin *XIII*, m.p. 69—71°C, $[\alpha]_D^{20}$ +1° (*c* 2·48).

c) *From the mesylate* VIII *with* sym-*collidine*: A solution of the mesylate *VIII* (400 mg) in *sym*-collidine (10 ml) was refluxed for 1 hour. The mixture was poured into water, the product taken into ether, and worked up. The residue (350 mg) was chromatographed on silica gel in ligroin to yield 285 mg of a product which on crysallisation from ethanol gave 205 mg of the olefin *XIII*, m.p. 68—70°C, $[\alpha]_D^{20}$ +4° (*c* 1·42).

The analyses were carried out in the Analytical Laboratory of this Institute under the direction of Dr J. Horáček. The infrared spectra were recorded by Mr P. Formánek under the direction of Dr J. Smolíková. The ^{1}H-NMR *spectra were recorded by Dr M. Buděšínský, Dr M. Synáčková and Dr J. Costa, Escuela de Quimica, Facultad de Ciencias, Universidad Central de Venezuela, the mass spectra by Dr A. Trka. Technical assistance was provided by Mrs J. Mašková.*

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