ON STEROIDS. CLI.* B-HOMOSTEROIDS. VIII.**

SOLVOLYTIC REACTIONS OF THE EPIMERIC 3-METHANESULPHONYLOXY-5,7-CYCLO-B-HOMOSTEROIDS

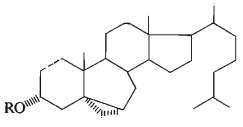
L.KOHOUT and J.FAJKOŠ

Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague 6

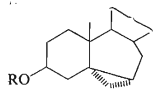
Received March 15th, 1972

Acetolyses of $C_{(3)}$ epimeric mesylates of the 5α,7α as well as 5β,7β-cyclo-B-homocholestane have been studied and the structure of the products established by chemical and spectral means.

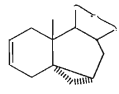
In our previous paper[1] we have described the synthesis of the epimeric 5,7-cyclo-B-homocholestanes with hydroxyl function in position 3 and established the stereochemistry of these compounds. They were of interest as a possible starting material for preparation of B-homosteroids with oxygen function at $C_{(7)}$. In analogy to the



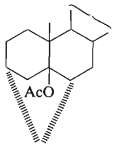
I, R = H
II, R = Mes
III, R = Ac



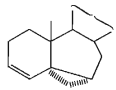
IV, R = H
V, R = Mes
VI, R = Ac
VII, R = Tos



VIII



IX

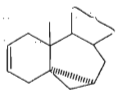


X

* Part CL: This Journal *38*, 583 (1973).
** Part VII: This Journal *38*, 279 (1973).

normal steroid series we may expect the solvolysis of the 3-mesylates of the 5α,7α--cyclo-B-homocholestane to give the B-homosteroid in good yield. In this paper we describe the behaviour of the four epimeric mesylates *II*, *V*, *XIII*, and *XVIII* under acetolytic conditions and prove the structures of the compounds obtained.

The acetolyses were carried out in glacial acetic acid under the presence of acetic anhydride and sodium acetate. When the 3α-methanesulphonyloxy derivative *II* was submitted to these conditions an olefin was obtained as the main product (Table I) and only small amounts of the hydroxy derivatives *I* and *IV* were isolated. In order to determine the position of the double bond in this olefin we synthesised the both isomeric olefins *VIII* and *X* from the tosylate *VII* by elimination in collidine. They were separated on silver coated silica gel the relation being 18 : 1 in favor of the olefin identical with the product of the acetolysis. Comparison of the NMR spectra of the olefins permitted assignment of structures. The olefinic protons in the main product showed chemical shift of 5·63 p.p.m. in contrast to the minor product where the signals were well separated (5·47 and 5·04 p.p.m.). This upfield shift of one of the olefinic protons in the minor product is evidently caused by shielding of the



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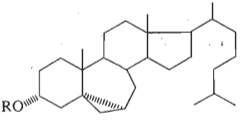

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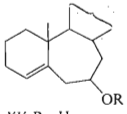
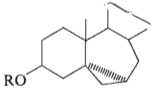
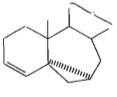


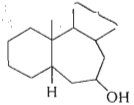
XV, R = H
XVI, R = Ac



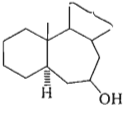
XVII, R = H
XVIII, R = Mes
XIX, R = Ac
XX, R = Tos



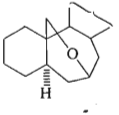
XXI



XXII



XXIII



XXIV

TABLE I

Solvolyses of the 3-Methanesulphonyloxy-5,7β-cyclo-B-homo-5β-cholestanes *II* and *V* (%)

Product	3α (*II*)	3β (*V*)
2,3-Olefin (*VIII*)	80	50
3,4-Olefin (*X*)	0	1
3α-Compound (*III*, *I* resp.)	5	16
3β-Compound (*VI*, *IV* resp.)	2	13
3α,6α-Endomethylene-5β-acetate (*IX*)	0	5

TABLE II

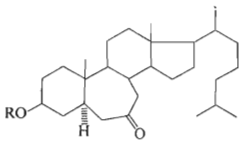
Solvolyses of the 3-Methanelsulphonyloxy-5,7α-cyclo-B-homo-5α-cholestanes *XIII* and *XVIII* (%)

Product	3α (*XIII*)	3β (*XVIII*)
2,3-Olefin (*XI*)	5	1
3,4-Olefin (*XXI*)	0	5
3α-Acetate (*XIV*)	2	3
3β-Acetate (*XIX*)	11	44
7β-Acetoxy-B-homo-4-cholestene (*XIV*)	75	32

$C_{(4)}$ proton with the cyclopropane protons and the minor product is therefore the 3,4-unsaturated compound *X*; the main product of the tosyloxy group elimination as well as the product of the acetolysis is the 2,3-isomer *VIII*.

More complex reaction mixture resulted on acetolysis of the 3β-mesylate *V*. (Table II). Here again the olefin *VIII* was the main component in the reaction mixture accompanied by the epimeric acetates *III* and *VI* and traces of the olefin *X* were detected. In addition to these compounds a new acetate was isolated in about 5% yield. Its structure was elucidated by spectral means. Mass spectrum showed a molecular peak of 442 units, NMR showed presence of a tertiary acetoxy group and absence of the cyclopropyl as well as of the olefinic protons in the molecule. In analogy to the B-norsteroid series[2] we assign the structure *IX* to this acetate. Like in the B-norsteroid series the Dreiding models of this five-cyclic structure show no considerable strain.

Similarly the epimeric mesylates *XIII* and *XVIII* of the 5α,7α-cyclo series were submitted to the acetolysis under identical conditions. In contrast to the 5β,7β-cyclo series where the products of elimination formed the main component in the reaction mixture, in this case the olefins originated in very low yields. They were prepared



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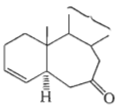
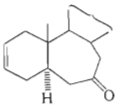
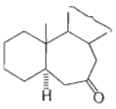


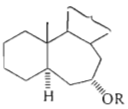
XXVII



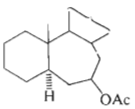
XXVIII



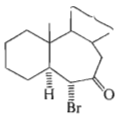
XXIX



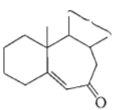
XXX, R = H
XXXI, R = Ac



XXXII



XXXIII



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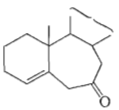
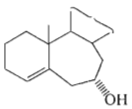


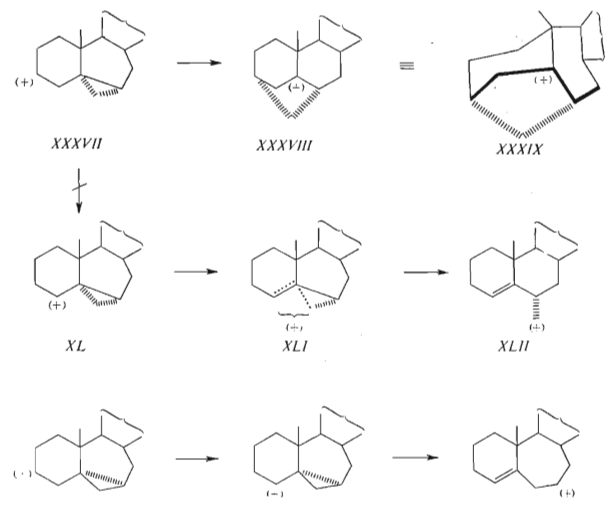
XXXV



XXXVI

in much better yields for comparision from the tosylate *XX* by reflux with collidine and their structures were elucidated again on the basis of the NMR spectra. Whereas the olefinic protons at $C_{(2)}$ and $C_{(3)}$ appeared as a multiplet at 5·96 p.p.m. the signals of the protons in the $\Delta^{3(4)}$-olefin were well separated (5·60 and 4·66 p.p.m.) reflecting a shielding effect by the cyclopropane ring. Next to the olefins *XI* and *XXI* and the epimeric acetates *XIV* and *XIX* a new acetate was isolated in good yields from the reaction mixtures after acetolyses of the both mesylates *XIII* and *XVIII*. NMR showed presence of a secondary acetoxy group and of one olefinic proton and absence of the cyclopropane ring. By analogy to the normal steroid series where the 3-mesylates of the 5α,7α-cyclo series afforded under similar conditions 7β-acetoxy-4-cholestene we expected this acetate to be the B-homosteroid derivative *XVI*.

This compound was therefore synthesised as follows: 3β-Hydroxy-B-homo-5α-cholestan-7-one (*XXV*) was transformed to the mesylate *XXVI* which on reaction with collidine afforded the olefins *XXVII* and *XXVIII* the relation being 3 : 1 in fa-



vor of the 3,4-isomer *XXVII*. Positions of the double bonds follow from the NMR spectra where the olefinic protons in the Δ^2-derivative appears at 5·57 p.p.m. as a multiplet whereas in the Δ^3-isomer the shielding of the $C_{(4)}$ proton with the 7-oxo group causes its upfield shift and the protons are well separated (5·71 p.p.m., 3-H; 5·18 p.p.m., 4-H). The both olefins were hydrogenated over palladium catalyst to yield the ketone *XXIX* which on bromination with bromine in acetic acid afforded the bromo ketone *XXXIII*. Position of the bromine atom in this bromo ketone follows from subsequent reactions and configuration from the NMR spectrum where the $C_{(6)}$ proton shows a large diaxial coupling (3·82 p.p.m., d, J = 9 Hz, 6β-H). Elimination of the bromine atom with lithium carbonate and lithium bromide in dimethylformamide at 120°C gave the α,β-unsaturated ketone *XXXIV* as the sole product. At higher temperatures the reaction led to a mixture of the ketones *XXXIV* and *XXXV*. This observation suggests the instability of the conjugated ketone which undergoes isomerisation when exposed to more drastic conditions. This was proved by experiments in which the conjugated ketone was treated under alkaline conditions which caused conversion into the 4,5-isomer *XXXV*. On metal hydride reduction

this 4,5-unsaturated ketone *XXXV* afforded two at $C_{(7)}$ epimeric alcohols *XXXVI* and *XV* one of them being identical with the alcohol obtained after hydrolysis of the acetate *XVI*. In order to determine the configuration of the hydroxyl group in this alcohol the double bond was hydrogenated to the saturated derivative *XXIII* which proved to be identical with one of the two alcohols obtained on reduction of the ketone *XXIX*; it has therefore 5α-configuration. Oxidation with lead tetraacetate afforded the 7β,19-oxide *XXIV* in excellent yield proving 7β-configuration of the hydroxyl group. The main product of the acetolyses of the 3-methanesulphonyloxy derivatives of the B-homo-5α,7α-cyclo series is therefore 7β-acetoxy-B-homo-4-cholestene (*XVI*).

These results are in close analogy to the findings obtained previously in the normal steroid series[2]. However some differences do exist. Whereas the acetolysis of the mesylate *V* gave only 5% of the endomethylene compound *IX*, analogous reaction in the normal steroid series gave the corresponding derivative as the main product. Also the acetolysis of the epimeric mesylate *II* proceeded differently: Whereas in the normal steroid series about 30% of 6α-acetoxymethyl-B-nor-4-cholestene were isolated, the analogous product the formation of which would proceed through the intermediates *XXXVII*–*XL*–*XLI*–*XLII* was not observed in this case. In the 5α,7α-cyclo series acetolyses of the both epimeric mesylates *XIII* and *XVIII* gave results analogous to those obtained in the normal steroids. The formation of the B-homo derivative *XVI* is explained by rearrangement of the ionic species *XLIII* to *XLIV* which is then stabilised by participation with the cyclopropane ring to give the cation *XLV* from which the product *XVI* originated. As expected this reaction represents an efficient route to preparation of B-homosteroids with the oxygen function at $C_{(7)}$.

Simple model consideration can not explain the difference in the behaviour of the mesylates of the normal and B-homo- 5β,7β-cyclo series under acetolytic conditions and further reactions of similar type are under investigation.

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°. IR spectra were recorded on the Zeiss UR 10 spectrometer. UV spectra were recorded on the CF 4 spectrometer in ethanol. The mass spectra were recorded on the mass spectrometer AEI MS 902. The NMR spectra were recorded on the Varian HA-100 instrument in deuteriochloroform unless otherwise stated with tetramethylsilane as internal reference. The chemical shift is given in p. p.m. The identity of samples prepared by different routes was checked by mixture melting point determination, by thin-layer chromatography, by optical rotation, and by infra-red spectra. Ligroin of b.p. 40—60°C was used as solvent. Working up of an ethereal solution means extraction with 5% HCl, water, 5% $NaHCO_3$, and water, drying with magnesium sulphate, and evaporation of the solvent.

5,7β-Cyclo-B-homo-5β-cholestan-3α-ol (*I*)

The corresponding zones from the preparative thin-layer chromatography after preparation of the 3β-epimer *IV* under *b*) containing the polar component were collected, eluted with water,

and the solvent was evaporated. The residue (19 mg) was crystallised from acetone to yield 10 mg of the alcohol *I*, m.p. 124–125°C, $[\alpha]_D^{20}$ −57·7° (*c* 0·73) in accordance with the literature[1].

3α-Methanesulphonyloxy-5,7β-cyclo-B-homo-5β-cholestane (*II*)

The alcohol *I* (156 mg) in pyridine (3 ml) was treated with methanesulphonyl chloride (0·3 ml) at +5°C and allowed to stand at room temperature for 18 h. The reaction mixture was decomposed with ice and the product taken into ether. The ethereal solution was worked up and the residue (160 mg) was crystallised from dichloromethane–methanol to afford 85 mg of the mesylate *II*, m.p. 113–115°C, $[\alpha]_D^{20}$ −41·4° (*c* 1·06); IR: 3070, 1342, 1180 cm^{-1}; NMR: 0·20 (mt, cyclopropane proton), 0·50 (mt, cyclopropane proton), 0·59 (s, 18-H), 0·85 (d, J = 6 Hz, 26-H and 27-H), 0·87 (d, J = 6 Hz 21-H), 1·04 (s, 19-H), 2·94 (s, 3α-mesylate), 4·99 (mt, 3β-H). For $C_{30}H_{50}O_3S$ (524·7) calculated: 73·43% C 10·27% H, 6·52% S; found: 73·49% C 10·11% H, 6·31% S.

3α-Acetoxy-5,7β-cyclo-B-homo-5β-cholestane (*III*)

Continued elution of the chromatography after isolation of the 3β-epimer *VI* with the same solvent mixture afforded fractions with the polar component. Combination and evaporation left 108 mg of a residue which on crystallisation from methanol yielded 72 mg of the acetate *III*, m.p. 136 to 137°C, $[\alpha]_D^{20}$ −44·5° (*c* 1·44) in accordance with the literature[1].

5,7β-Cyclo-B-homo-5β-cholestan-3β-ol (*IV*)

a) The mesylate *V* (48 mg) in tetrahydrofuran (10 ml) was refluxed with a solution of lithium-aluminium hydride (50 mg) in the same solvent for 1 h. The reaction mixture was decomposed with ethyl acetate and water, the product extracted into ether and the ethereal solution was worked up. The residue (46 mg) was chromatographed preparatively on two plates of silica gel (20 × 20 cm) in ligroin–ether (7 : 3). The corresponding zones were collected extracted with ether, and the solvent was evaporated. The residue (41 mg) was crystallised from acetone to yield 25 mg of the alcohol *IV*, m.p. 158–159°C, $[\alpha]_D^{20}$ −46° (*c* 1·48) in agreement with the literature[1]. *b*) Elution of the chromatography after preparation of the olefin *VIII* under *a*) with ligroin–ether (19 : 1) afforded after working up and evaporation 45 mg of a product which was dissolved in methanol (8·5 ml) and refluxed for 2 h with a solution of potassium carbonate (100 mg) in water (1·5 ml). Methanol was removed under reduced pressure, the residue diluted with water, and the product taken into ether. The ethereal layer was washed with water, dried, and evaporated. The residue, containing according to the thin-layer chromatography two components, was chromatographed preparatively on two plates of silica gel (20 × 20 cm) in ligroin–ether (7 : 3). The zones with the lipophilic component were collected and eluted with ether. Evaporation and crystallisation from methanol gave 8 mg of the alcohol *IV*, m.p. 159–160°C, $[\alpha]_D^{20}$ −47·5° (*c* 0·43).

3β-Methanesulphonyloxy-5,7β-cyclo-B-homo-5β-cholestane (*V*)

A solution of the alcohol *IV* (458 mg) in pyridine (8 ml) was treated at +5°C with methanesulphonyl chloride (0·7 ml) and allowed to stand at room temperature for 18 h. The reaction mixture was decomposed with ice, diluted with water, the product taken into ether, and the ethereal solution was worked up. The residue was crystallised from chloroform–methanol to yield 365 mg of the mesylate *V*, m.p. 114·5–115·5°C, $[\alpha]_D^{20}$ −44·7° (*c* 0·90); IR: 3060, 1369, 1343, 1178, 935 cm^{-1}; NMR: 0·10–0·50 (mt, cyclopropane protons), 0·59 (s, 18-H), 0·84 (d, J = 6 Hz,

26-H and 27-H), 0·87 (d, $J = 6$ Hz, 21-H), 1·08 (s, 19-H), 2·94 (s, 3β-mesylate), 4·60—4·90 (mt, 3α-H). For $C_{30}H_{50}O_3S$ (490·7) calculated: 73·43% C, 10·27% H, 6·52% S; found: 73·59% C, 10·31% H, 6·73% S.

3β-Acetoxy-5,7β-cyclo-B-homo-5β-cholestane (*VI*)

Elution of the chromatography after isolation of the acetate *IX* with ligroin–ether (99 : 1), combination of the corresponding fractions evaporation of the solvent, and crystallisation from methanol yielded 65 mg of the acetate *VI*, m.p. 120—121°C, $[\alpha]_D^{20}$ −51·9° (*c* 1·06) in agreement with the literature[1].

3β-Toluenesulphonyloxy-5,7β-cyclo-B-homo-5β-cholestane (*VII*)

A solution of the alcohol *IV* (1·66 g) in pyridine (16 ml) was treated with toluenesulphonyloxy chloride (1·66 g) and allowed to stand at room temperature for 18 h. The reaction mixture was then poured on ice, water was added, and the product extracted with ether. The ethereal solution was worked up and the residue was crystallised from chloroform–methanol to give 800 mg of the tosylate *VII*, m.p. 143—145°C, $[\alpha]_D^{20}$ −44·9° (*c* 0·93); IR: 3060, 1600, 1496, 1371, 1190, 1180 cm^{-1}; NMR: 0·01 (q, $J = 9$ Hz, $J = 4$ Hz, one cyclopropane proton), 0·30 (mt, one cyclopropane proton), 0·59 (s, 18-H), 0·86 (d, $J = 6$ Hz, 26-H and 27-H), 0·88 (d, $J = 6$ Hz, 21-H), 1·05 (s, 19-H). 2·42 (broad s, methyl of the tosylate), 4·51 (broad mt, 3α-H), 7·31 and 7·77 (aromatic protons). For $C_{35}H_{54}O_3S$ (554·9) calculated: 75·76% C, 9·81% H, 5·78% S; found: 75·62% C, 9·86% H, 6·08% S.

5,7β-Cyclo-B-homo-5β-cholest-2-ene (*VIII*)

a) The mesylate *II* (500 mg) in acetic acid (12·5 ml) and acetic anhydride (1·25 ml) was refluxed with anhydrous sodium acetate (500 mg) for 5 h. Water was then added to decompose the excess anhydride and the reaction mixture was extracted with ether. The ethereal solution was washed with water, a sodium hydrogen carbonate solution, water, dried, and evaporated. The residue (500 mg) was chromatographed on a silica gel column (50 g) in ligroin–ether (19 : 1). Fractions containing the most lipophilic component were combined, evaporated, and the residue (290 mg) was crystallised from ethanol to yield 220 mg of the olefin *VIII*, m.p. 83—84°C, $[\alpha]_D^{20}$ −3·7° (*c* 1·65); IR (CS_2): 3060, 3015, 1648, 658 cm^{-1}; NMR: 0·10 (q, $J = 4{\cdot}5$ Hz, $J = 9$ Hz, one cyclopropane proton), 0·26 (td, $J = 1{\cdot}5$ Hz, $J = 4{\cdot}5$ Hz, one cyclopropane proton), 0·60 (s, 18-H), 0·84 (d, $J = 6$ Hz, 26-H and 27-H), 0·88 (d, $J = 6$ Hz, 21-H), 1·06 (s, 19-H), 2·53 (d mt, $J = 16$ Hz, one of the allylic protons), 5·63 (mt, 2-H and 3-H). For $C_{28}H_{46}$ (382·7) calculated: 87·88% C, 12·12% H; found: 87·73% C, 12·43% H. *b*) Continued elution of the chromatography after preparation of the olefin *X* under *a*) with n-heptane–ether (99 : 1), working up of the corresponding fractions, and evaporation of the solvent left 290 mg of a product which on crystallisation from ethanol gave 230 mg of the olefin *VIII*, m.p. 83—84°C, $[\alpha]_D^{20}$ −6·7° (*c* 1·68). *c*) Elution of the chromatography after isolation of the olefin *X* under *b*) with n-heptane–ether (99 : 1) gave after working up and evaporation 900 mg of a product which on crystallisation from ethanol yielded 685 mg of the olefin *VIII*, m.p. 83—84°C, $[\alpha]_D^{20}$ −7·4° (*c* 2·75).

3α,6α-Endomethylene-5-acetoxy-5β-cholestane (*IX*)

Fractions of the chromatography after isolation of the olefin *X* under *a*) containing the polar components were combined and evaporated. The residue (240 mg) was chromatographed over

silica gel (25 g) in ligroin–ether (99·1). The corresponding fractions were combined, evaporated, and the residue (37 mg) was crystallised from methanol to yield 22 mg of the acetate *IX*, m.p. 129—130°C, $[\alpha]_D^{20}$ +33° (*c* 0·61); IR: 1 730, 1 246 cm^{-1}; mass spectrum: M^+ 442; NMR: 0·64 (s, 18-H), 0·74 (d, *J* = 6·5 Hz, 26-H and 27-H), 0·87 (d, *J* = 6 Hz, 21-H), 1·00 (s, 19-H), 1·95 (s, 5β-acetate). For $C_{30}H_{50}O_2$ (442·7) calculated: 81·39% C, 11·38% H; found: 81·45% C, 11·50% H.

5,7β-Cyclo-B-homo-5β-cholest-3-ene (*X*)

a) The mesylate *V* (800 mg) was solvolysed in acetic acid (20 ml) and acetic anhydride (2 ml) under the presence of freshly fused sodium acetate (800 mg) as given for the preparation of the olefin *VIII* under *a*). Similar working up afforded 760 mg of an oil which was chromatographed on a silica gel column (20 g) in ligroin–ether (19 : 1) to separate the polar (acetate *IX*) and lipophilic components (olefins *VIII* and *X*). Fractions containing the olefins were combined, evaporated, and the residue (466 mg) was chromatographed over silver-coated silica gel (20%; 40 g) in n-heptane–ether (99 : 1). Fractions containing the lipophilic olefin were combined, evaporated, and the residue was crystallised from ethanol to afford 8·5 mg of the olefin *X*, m.p. 102—104°C, $[\alpha]_D^{20}$ −149·7° (*c* 0·41); IR (CS_2): 3 060, 1 640, 700 cm^{-1}; NMR: 0·28 (q, *J* = 5 Hz, *J* = 9 Hz, one cyclopropane proton), 0·39 (t, *J* = 5 Hz, one cyclopropane proton), 0·62 (s, 18-H), 0·85 (d, *J* = 6·5 Hz, 26-H and 27-H), 0·88 (d, *J* = 6 Hz, 21-H), 1·03 (s, 19-H), 5·04 (dt, *J* = 10 Hz, *J* = 2 Hz, *J* = 2 Hz, 4-H), 5·47 (mt, 3-H). For $C_{28}H_{46}$ (382·7) calculated: 87·88% C, 12·12% H; found: 88·02% C, 12·20% H. *b*) A solution of the tosylate *VII* (1·45 g) in *sym*-collidine (25 ml) was refluxed for 2 h in a nitrogen atmosphere. The reaction mixture was cooled off to room temperature, poured into water, and the product taken into ether. The ethereal solution was worked up and the residue (1·3 g) was chromatographed over silver-coated silica gel (20%; 100 g) in n-heptane–ether (99 : 1). Fractions containing the lipophilic component were combined, evaporated, and the residue (51 mg) was crystallised from ethanol to yield 35 mg of the olefin *X*, m.p. 103—104°C, $[\alpha]_D^{20}$ −150° (*c* 0·88).

5,7α-Cyclo-B-homo-5α-cholest-2-ene (*XI*)

a) The tosylate *XX* (1·72 g) in *sym*-collidine (30 ml) was refluxed for 2 h under nitrogen. Collidin was then distilled off under reduced pressure, the residue was diluted with water and 5% HCl, and the product was isolated with ether. The ethereal solution was worked up, and the residue (1·6 g) was chromatographed over silica gel (900 g) in n-heptane. Fractions containing the lipophilic product were combined, evaporated, and the residue was crystallised from methanol to yield 830 mg of the olefin *XI*, m.p. 57—59°C, $[\alpha]_D^{20}$ +4·9° (*c* 1·14); IR (CS_2): 3·060, 3045, 1 635, 701 cm^{-1}; NMR: 0·10 (q, *J* = 8 Hz, *J* = 5 Hz, one cyclopropane proton), 0·25 (t, *J* = = 4·5 Hz, one cyclopropane proton), 0·59 (s, 18-H), 0·81 (s, 19-H), 0·84 (d, *J* = 6 Hz, 26-H and 27-H), 0·88 (d, *J* = 6 Hz, 21-H), 5·96 (mt, olefinic protons). For $C_{28}H_{46}$ (382·7) calculated: 87·88% C, 12·12% H; found: 88·08% C, 11·98% H. *b*) The mesylate *XVIII* (1·85 g) was solvolysed in acetic acid (48 ml) and acetic anhydride (4·8 ml) under the presence of freshly fused sodium acetate (1·85 g) as given for the preparation of the olefin *VIII* under *a*). Similar working up afforded 1·5 g of an oil which was chromatographed over silica gel (110 g) in ligroin–ether (99 : 1) to separate the olefins *XI* and *XXI* and the acetate *XVI*. Fractions containing the olefins were combined, evaporated, and the residue was chromatographed over silver-coated silica gel (20%; 10 g) in n-heptane–ether (99 : 1). Fractions containing the lipophilic olefin were worked up and the residue (16 mg) was crystallised from ethanol to yield 8·5 mg of the olefin *XI*, m.p. 55—58°C, $[\alpha]_D^{20}$ +4·6° (*c* 0·82). *c*) The mesylate *XIII* (600 mg) was solvolysed in acetic acid (15 ml) and acetic anhydride (1·5 ml) under the presence of freshly fused sodium acetate (600 mg) as described

for the preparation of the olefin *VIII* under *a*). Similar working up afforded 640 mg of an oil which was chromatographed over silica gel (65 g) in ligroin–ether (99 : 1). Fractions containing the olefin were combined, evaporated, and the residue was crystallised from ethanol to yield 20 mg of the olefin *XI*, m.p. 57–59°C, $[\alpha]_D^{20}$ +4·1° (*c* 0·45).

3α-Methanesulphonyloxy-5,7α-cyclo-B-homo-5α-cholestane (*XIII*)

A solution of the alcohol *XII* (172 mg) in pyridine (3 ml) was treated at +5°C with methanesulphonyl chloride (0·3 ml) and allowed to stand at room temperature for 18 h. The reaction mixture was decomposed with ice, diluted with water, and the product extracted into ether. Working up gave 175 mg of a residue which on crystallisation from dichloromethane–methanol yielded 105 mg of the mesylate *XIII*, m.p. 130–132°C, $[\alpha]_D^{20}$ 0° (*c* 1·92); IR: 3060, 1343, 1180 cm^{-1}; NMR: −0·02 (mt, one cyclopropane proton), 0·25 (mt, one cyclopropane proton), 0·61 (s, 18-H), 0·81 (s, 19-H), 0·84 (d, J = 6 Hz, 26-H and 27-H), 0·86 (d, J = 6 Hz, 21-H), 2·96 (s, 3α-mesylate), 4·95 (broad mt, 3β-H). For $C_{30}H_{50}O_3S$ (490·7) calculated: 73·43% C, 10·27% H, 6·52% S; found: 73·51% C, 9·82% H, 6·59% S.

3α-Acetoxy-5,7α-cyclo-B-homo-5α-cholestane (*XIV*)

a) Elution of the chromatography after isolation of the acetate *XIX* under *a*) with ligroin–ether (99 : 1) afforded fractions containing the acetate *XIV*. Combination and evaporation left 52 mg of a product which on crystallisation from methanol yielded 33 mg of the acetate *XIV*, m.p. 67–68°C, $[\alpha]_D^{20}$ +4·7° (*c* 1·16) in agreement with the literature[1]. *b*) Elution of the chromatography after isolation of the acetate *XIX* under *b*) with ligroin–ether (33 : 1), working up of the corresponding fraction, and crystallisation from methanol gave 11 mg of the acetate *XIV*, m.p. 65–68°C, $[\alpha]_D^{20}$ +3·5° (*c* 0·51).

7β-Hydroxy-B-homo-4-cholestene (*XV*)

a) The acetate *XVI* (260 mg) in methanol (17 ml) was refluxed with a solution of potassium carbonate (240 mg) in water (3 ml) for 4 h. Methanol was removed under reduced pressure, the product taken into ether, the ethereal solution was washed with water, dried, and evaporated. The residue was chromatographed over silica gel (10 g) in ligroin–ether (9 : 1). The corresponding fractions were combined, and evaporated, to yield 207 mg of the oily alcohol *XV*; $[\alpha]_D^{20}$ −24·5° (*c* 0·62); IR: 3615, 3030, 1655, 1031, 998 cm^{-1}; NMR: 0·68 (s, 18-H), 0·84 (d, J = 6 Hz, 26-H and 27-H), 0·89 (d, J = 6 Hz, 21-H), 0·96 (s, 19-H), 3·89 (broad mt, 7α-H), 5·27 (q, J = 2·5 Hz, J = 6 Hz, 4-H). For $C_{28}H_{48}O$ (400·7) calculated: 83·93% C, 12·08% H; found: 84·12% C, 12·06% H. *b*) A solution of lithiumaluminium hydride (1 g) in tetrahydrofuran (20 ml) was added to a solution of the ketone *XXXV* (450 mg) in the same solvent (100 ml) and allowed to stand at room temperature for 10 min. The excess hydride was decomposed ethyl acetate, water was added, and the product was isolated with ether. The ethereal solution was worked up as usual and the residue (450 mg) was chromatographed preparatively on 10 silica gel plates (20 × 20 cm) in ligroin–ether (3 : 1). Zones with the lipophilic component were collected, the product eluted with ether, and the solvent was evaporated to yield 273 mg of the oily alcohol *XV*, $[\alpha]_D^{20}$ −24·1° (*c* 1·03). *c*) Tri-tert-butoxyaluminium hydride (1 g) was added to a solution of the ketone *XXXV* (500 mg) in tetrahydrofuran (20 ml). After 30 min at room temperature the reaction mixture was decomposed with water and 2% hydrochloric acid, the product was isolated with ether, and the ethereal solution was worked up as usual. The residue (500 mg) was chromatographed on a si-

lica gel column (50 g) in ligroin–ether (19 : 1). The corresponding fractions gave after combination and evaporation 390 mg of the oily alcohol *XV*, $[\alpha]_D^{20}$ −23·7° (*c* 1·17).

7β-Acetoxy-B-homo-4-cholestene (*XVI*)

a) The alcohol *XV* (113 mg) was acetylated with acetic anhydride (0·6 ml) in pyridine (1 ml) for 20 h at room temperature. The reaction mixture was decomposed with ice, the product extracted with ether, and the ethereal solution was worked up. The residue (120 mg) was crystallised from ethanol to give 78 mg of the acetate *XVI*, m.p. 132–134°C, $[\alpha]_D^{20}$ −19·6° (*c* 3·72), IR: 1738, 1248, 1023 cm^{-1}; mass spectrum: M^+ 442; NMR: 0·69 (s, 18-H), 0·85 (d, $J = 6$ Hz; 26-H and 27-H), 0·88 (d, $J = 6$ Hz, 21-H), 0·97 (s, 19-H), 1·99 (s, 7β-$COOCH_3$), 4·91 (broad mt, 7α-H), 5·35 (t, $J = 3$ Hz, 4-H). For $C_{30}H_{50}O_2$ (442·7) calculated: 81·39% C, 11·38% H; found: 81·28% C, 11·41% H. *b*) Continued elution of the chromatography after preparation of the olefin *XI* under *b*) with ligroin–ether (99 : 1) and working up of the corresponding fractions gave after evaporation of the solvent 497 mg of a product which on crystallisation from ethanol yielded 280 mg of the acetate *XVI*, m.p. 131–134°C, $[\alpha]_D^{20}$ −20·0° (*c* 1·11). *c*) Elution of the chromatography after isolation of the olefin *XI* under *c*) with ligroin–ether (99 : 1) working up and evaporation of the solvent left 380 mg of a residue which was crystallised from ethanol to yield 200 mg of the acetate *XVI*, m.p. 133–134°C, $[\alpha]_D^{20}$ −21·7° (*c* 2·52).

5,7α-Cyclo-B-homo-5α-cholestan-3β-ol (*XVII*)

A solution of lithiumaluminium hydride (40 mg) in tetrahydrofuran (5 ml) was added to a solution of the mesylate *XVIII* (40 mg) in the same solvent (10 ml) and refluxed for 1 h. The excess hydride was decomposed with ethyl acetate and water, the product was isolated with ether, and the ethereal solution was worked up in the usual way. The residue after evaporation of ether (40 mg) was chromatographed preparatively on two plates of silica gel (20 × 20 cm) in ligroin–ether (7 : 3). The corresponding zones were collected, the product eluted with ether, solvent evaporated, and the residue (36 mg) was crystallised from acetone to yield 18 mg of the alcohol *XVII*, m.p. 108–110°C, $[\alpha]_D^{20}$ −3·1° (*c* 1·59) in agreement with the literature[1].

3β-Methanesulphonyloxy-5,7α-cyclo-B-homo-5α-cholestane (*XVIII*)

Methanesulphonyl chloride (0·6 ml) was added at +5°C to a solution of the alcohol *XVII* (409 mg) in pyridine (5 ml) and allowed to stand at room temperature for 18 h. The reaction mixture was decomposed with ice, the product taken into ether, and the ethereal solution was worked up. The residue (420 mg) was crystallised from chloroform–methanol to yield 235 mg of the mesylate *XVIII*, m.p. 77–79°C, $[\alpha]_D^{20}$ +10·4° (*c* 0·76); IR: 3065, 1368, 1334, 1180, 919 cm^{-1}; NMR: −0·10 to 0·10 (mt, one cyclopropane proton), 0·25–0·45 (mt, one cyclopropane proton), 0·61 (s, 18-H), 0·85 (d, $J = 6$ Hz, 26-H and 27-H), 0·87 (s, 19-H), 0·88 (d, $J = 6$ Hz, 21-H), 2·95 (s, 3β-mesylate), 4·86 (mt, 3α-H). For $C_{30}H_{50}O_3S$ (490·7) calculated: 73·43% C, 10·27% H, 6·52% S; found: 73·70% C, 10·12% H, 6·41% S.

3β-Acetoxy-5,7α-cyclo-B-homo-5α-cholestane (*XIX*)

a) Elution of the chromatography after isolation of the acetate *XVI* under *b*) with ligroin–ether (99 : 1) afforded 681 mg of a product which on crystallisation from methanol gave 550 mg of the acetate *XIX*, m.p. 85–86°C, $[\alpha]_D^{20}$ −2·7° (*c* 1·93) in accordance with the literature[1]. *b*) Elution

of the chromatography after preparation of the acetate *XVI* under *c*) with ligroin–ether (33 : 1) gave 54 mg of the acetate *XIX*, m.p. 86–87°C (methanol), $[\alpha]_D^{20}$ −1·8° (*c* 0·84).

3β-Toluenesulphonyloxy-5,7α-cyclo-B-homo-5α-cholestane (*XX*)

A solution of the alcohol *XVII* (2·07 g) in pyridine (20 ml) was treated with *p*-toluenesulphonyl chloride (2·07 g) and allowed to stand at room temperature for 18 h. The reaction mixture was decomposed with ice and water, and the product was taken into chloroform–benzene. Usual working up and crystallisation from chloroform–methanol gave 1·2 g of the tosylate *XX*, m.p. 99–100°C, $[\alpha]_D^{20}$ +1·4 (*c* 1·47); IR: 3060, 1608, 1496, 1190, 1180 cm^{-1}; NMR: −0·10 (q, J = 10 Hz, J = 6 Hz, one cyclopropane proton), 0·27 (mt, one cyclopropane proton), 0·60 (s, 18-H), 0·84 (s, 19-H), 0·85 (d, J = 6 Hz, 26-H and 27-H), 0·87 (d, J = 6 Hz, 21-H), 2·43 (broad s, methyl of the tosylate), 4·70 (broad mt, 3α-H), 7·31 and 7·77 (AA'BB' pattern, J = 8·5 Hz, aromatic protons). For $C_{35}H_{54}O_3S$ (554·9) calculated: 75·76% C, 9·81% H, 5·78% S; found: 75·86% C, 9·98% H, 6·05% S.

5,7α-Cyclo-B-homo-5α-cholest-3-ene (*XXI*)

a) Elution of the chromatography after isolation of the olefin *XI* under *a*) with n-heptane, working up of the corresponding fractions, and evaporation of the solvent left 1·03 g of a product which on crystallisation from ethanol yielded 830 mg of the olefin *XXI*, m.p. 71·5–72·5°C, $[\alpha]_D^{20}$ +13·4° (*c* 2·09); IR (CS_2): 3070, 3010, 1650, 707 cm^{-1}; NMR: 0·14 (q, J = 4 Hz, J = 8 Hz, one cyclopropane proton), 0·63 (s, 18-H), 0·81 (s, 19-H), 0·84 (d, J = 6 Hz, 26-H and 27-H), 0·87 (d, J = 6 Hz, 21-H), 4·66 (d mt, J = 10 Hz, 4-H), 5·60 (mt, 3-H). For $C_{28}H_{46}$ (382·7) calculated: 87·88% C, 12·12% H; found: 87·78% C, 12·05% H. *b*) Elution of the chromatography of the olefinic fraction after isolation of the olefin *XI* under *b*) with n-heptane–ether (99 : 1) afforded after combination of the corresponding fraction and evaporation of the solvent 65 mg of a product which on crystallisation from ethanol gave 51 mg of the olefin *XXI*, m.p. 71–73°C, $[\alpha]_D^{20}$ +11·8° (*c* 0·84).

B-Homo-5β-cholestan-7β-ol (*XXII*)

The zones from the preparative thin-layer chromatography of the alcohol *XXIII* under *b*) containing the polar alcohol were collected, eluted with ether, and ether was distilled off leaving 56 mg of the oily alcohol *XXII*, $[\alpha]_D^{20}$ +36·7° (*c* 1·84); IR: 3610, 1035, 1002, 994 cm^{-1}; NMR: 0·66 (s, 18-H), 0·86 (d, J = 6 Hz, 26-H and 27-H), 0·90 (d, J = 6 Hz, 21-H), 0·96 (s, 19-H), 3·95 (broad mt, 7α-H). For $C_{28}H_{50}O$ (402·7) calculated: 83·51% C, 12·52% H; found: 83·45% C, 12·10% H.

B-Homo-5α-cholestan-7β-ol (*XXIII*)

a) Tri-tert-butoxyaluminium hydride (800 mg) was added to a solution of the ketone *XXIX* (400 mg) in tetrahydrofuran (10 ml) and allowed to stand at room temperature for 1 h. The reaction mixture was poured into 1% hydrochloric acid, the product was extracted with ether, and the ethereal solution was worked up. The residue (400 mg) was chromatographed preparatively on 10 plates of silica gel (20 × 20 cm) in ligroin–ether (3 : 1). The zones containing the lipophilic component were collected, the product was eluted with ether, and the solvent was distilled off to leave 187 mg of the oily alcohol *XXIII*, $[\alpha]_D^{20}$ +21·6° (*c* 1·58); IR: 3610, 1038, 1013 cm^{-1}; NMR: 0·68 (s, 18-H), 0·84 (s, 19-H), 0·86 (d, J = 6 Hz, 26-H and 27-H), 0·90 (d, J = 6 Hz,

21-H), 3·97 (broad mt, 7α-H). For $C_{28}H_{50}O$ (402·7) calculated: 83·51% C, 12·52% H; found: 83·34% C, 12·40% H. *b*) The olefin *XV* (160 mg) in ethyl acetate (5 ml) and ethanol (5 ml) was hydrogenated for 4 h over 5% $Pd/CaCO_3$ catalyst (160 mg). Catalyst was filtered off, washed with ether, the filtrate was evaporated, and the residue (160 mg) was chromatographed preparatively on 6 plates of silica gel (20 × 20 cm) in ligroin–ether (3 : 1). The zones with the lipophilic component were collected, eluted with ether, and the solvent was distilled off to yield 45 mg of the alcohol *XXIII*, $[\alpha]_D^{20}$ +20·7° (*c* 1·36).

7β,19-Oxido-B-homo-5α-cholestane (*XXIV*)

The alcohol *XXIII* (65 mg) was dissolved in benzene (8 ml), 1 ml of the solvent was distilled off, the solution was treated with lead tetraacetate (160 mg) and refluxed under stirring and irradiation (500 W Nitraphot lamp) for 1 h. After cooling off to room temperature the solid was filtered off, washed with ether, and the filtrate was washed with water, 5% sodium hydrogen carbonate, water, dried, and evaporated. The residue (62 mg) was chromatographed preparatively on 2 silica gel plates (20 × 20 cm) in ligroin–ether (9 : 1). Collection of the corresponding zones, elution with ether, and crystallisation of the product from methanol afforded 37 mg of the oxide *XXIV*, m.p. 71–72°C, $[\alpha]_D^{20}$ +8·3° (*c* 1·69); IR: 1 089 cm^{-1}; NMR: 0·71 (s, 18-H), 0·86 (d, J = 6 Hz, 26-H and 27-H), 0·89 (d, J = 6 Hz, 21-H), 3·69 and 3·86 (two d, J = 11 Hz, 19-H), 4·02 (mt, 7α-H). For $C_{28}H_{48}O$ (400·7) calculated: 83·93% C, 12·08% H; found: 84·05% C, 12·07% H.

3β-Methanesulphonyloxy-B-homo-5α-cholestan-7-one (*XXVI*)

A solution of the alcohol[3] *XXV* (450 mg) in pyridine (3 ml) was treated at +5°C with methanesulphonyl chloride (0·9 ml) and allowed to stand at room temperature for 18 h. The reaction mixture was decomposed with ice, treated with water, and the product was isolated with ether, and worked up as usual. The residue was dissolved in benzene, the solution was filtered over 1 g of activated charcoal, and the solvent was evaporated. The residue was crystallised from methanol to yield 350 mg of the mesylate *XXVI*, m.p. 143–144°C, $[\alpha]_D^{20}$ −27·8° (*c* 2·30); IR: 1705, 1365, 1345, 1178 cm^{-1}; NMR: 0·65 (s, 18-H), 0·81 (s, 19-H), 0·85 (d, J = 6 Hz, 26-H and 27-H), 0·89 (d, J = 6 Hz, 21-H), 2·99 (s, 3β-mesylate), 4·59 (broad mt, 3α-H). For $C_{30}H_{50}O_4S$ (506·7) calculated: 71·11% C, 9·95% H, 6·32% S; found: 71·44% C, 10·12% H, 6·71% S.

7-Oxo-B-homo-5α-cholest-3-ene (*XXVII*)

The mesylate *XXVI* (4 g) in *sym*-collidine (20 ml) was refluxed in a nitrogen atmosphere for 90 min. Collidine was then distilled off under reduced pressure, the residue was treated with water, and the product taken into ether. Working up and evaporation left 3·8 g of a product which was chromatographed over silica gel (380 g) in ligroin–ether (24 : 1). Fractions containing the lipophilic component were combined, evaporated, and the residue (2·16 g) was crystallised from methanol to yield 1·82 g of the olefin *XXVII*, m.p. 70–72°C, $[\alpha]_D^{20}$ +28·8° (*c* 0·77); IR: 1 700, 1 665 cm^{-1}; NMR: 0·64 and 0·67 (two s, 18-H and 19-H), 0·85 (d, J = 6 Hz, 26-H and 27-H), 0·88 (d, J = 6 Hz, 21-H), 2·10–2·70 (mt, 6-H and 7a-H), 5·18 (d mt, J = 11 Hz, 4-H), 5·71 (mt, 3-H). For $C_{28}H_{46}O$ (398·6) calculated: 84·35% C, 11·63% H; found: 84·99% C, 11·81% H.

7-Oxo-B-homo-5α-cholest-2-ene (*XXVIII*)

Elution of the chromatography from the foregoing experiment with the same solvent mixture afforded fractions with the polar component. Working up and evaporation left 715 mg of a pro-

duct which on crystallisation from methanol gave 580 mg of the olefin *XXVIII*, m.p. 108—109°C, $[\alpha]_D^{20}$ −42·8° (*c* 1·04); IR: 1705, 1675 cm^{-1}; NMR: 0·68 (s, 18-H), 0·86 (d, J = 6 Hz, 26-H and 27-H), 0·89 (s, 19-H), 0·90 (d, J = 6 Hz, 21-H), 5·57 (mt, 2-H and 3-H). For $C_{28}H_{46}O$ (398·6) calculated: 84·35% C, 11·63% H; found: 84·09% C, 11·83% H.

B-Homo-5α-cholestan-7-one (*XXIX*)

a) The olefin *XXVII* (390 mg) in ethyl acetate (10 ml) and ethanol (10 ml) was hydrogenated over 5% $Pd/CaCO_3$ catalyst (400 mg) for 2 h at room temperature. The catalyst was filtered off, washed with ether, and the filtrate was evaporated to dryness. The residue (390 mg) was crystallised from methanol to yield 325 mg of the ketone *XXIX*, m.p. 75—77°C (recrystallisation at 60°C), $[\alpha]_D^{20}$ −22·5° (*c* 1·31); IR: 1704 cm^{-1}; NMR: 0·65 (s, 18-H), 0·77 (s, 19-H), 0·85 (d, J = 6 Hz, 26-H and 27-H), 0·88 (d, J = 6 Hz, 21-H). For $C_{28}H_{48}O$ (400·7) calculated: 83·93% C, 12·08% H; found: 83·77% C, 12·23% H. *b*) The olefin *XXVIII* (475 mg) in ethyl acetate (10 ml) and ethanol (10 ml) was hydrogenated over 5% $Pd/CaCO_3$ (475 mg) as given in the foregoing experiment. Similar working up and crystallisation from methanol gave 390 mg of the ketone *XXIX*, m.p. 75—77°C, $[\alpha]_D^{20}$ −24·6° (*c* 1·49). *c*) The alcohol *XXX* (60 mg) in acetone (10 ml) was treated with excess Jones' reagent and after 5 min at room temperature methanol was added to remove the excess oxidising agent. The reaction mixture was treated with water, the product extracted into ether, the ethereal solution was washed with 5% $NaHCO_3$, water, dried, and evaporated. The residue (60 mg) on crystallisation from methanol gave 45 mg of the ketone *XXIX*, m.p. 74—76°C, $[\alpha]_D^{20}$ − 21·2° (*c* 1·11). *d*) The alcohol *XXIII* (35 mg) in acetone (2 ml) was oxidised with Jones' reagent as described in the foregoing experiment. Similar working up and crystallisation from methanol yielded 22 mg of the ketone *XXIX*, m.p. 74—77°C, $[\alpha]_D^{20}$ −21·0° (*c* 1·19).

B-Homo-5α-cholestan-7α-ol (*XXX*)

Elution of the chromatography after isolation of the 7β-epimer *XXIII* under *a*) with ligroin–ether (3 : 1), and working up of the corresponding fractions left 154 mg of a product which on crystallisation from ligroin gave 115 mg of the alcohol *XXX*, m.p. 146—147°C, $[\alpha]_D^{20}$ +15·8° (*c* 0·89); IR: 3610, 1022 cm^{-1}; NMR: 0·64 (s, 18-H), 0·78 (d, J = 6 Hz, 26-H and 27-H), 0·88 (s, 19-H), 0·88 (d, J = 6 Hz, 21-H), 3·70—4·10 (mt, 7β-H). For $C_{28}H_{50}O$ (402·7) calculated: 83·51% C, 12·52% H; found: 83·11% C, 12·73% H.

7α-Acetoxy-B-homo-5α-cholestane (*XXXI*)

The alcohol *XXX* (64 mg) was acetylated with acetic anhydride (3 ml) in pyridine (5 ml) for 2 days at room temperature. The reaction mixture was decomposed with ice, treated with water, and the product taken into ether. Working up and evaporation of the solvent left 70 mg of the oily acetate *XXXI*, $[\alpha]_D^{20}$ +6·0° (*c* 0·95); IR: 1732, 1250, 1020 cm^{-1}; NMR: 0·64 (s, 18-H), 0·77 (s, 19-H), 0·86 (d, J = 6 Hz, 26-H and 27-H), 0·89 (d, J = 6 Hz, 21-H), 1·97 (s, 7α-acetate), 4·90 (broad mt, 7β-H). For $C_{30}H_{50}O_2$ (442·7) calculated: 81·39% C, 11·38% H; found: 81·60% C, 11·42% H.

7β-Acetoxy-B-homo-5α-cholestane (*XXXII*)

The alcohol *XXIII* (108 mg) was acetylated with acetic anhydride (0·6 ml) in pyridine (1 ml) for 18 h at room temperature. Usual working up and evaporation of the solvent left 115 mg

of the oily acetate *XXXII*, $[\alpha]_D^{20}$ +6·8° (*c* 1·09); IR: 1735, 1248, 1022 cm^{-1}; NMR: 0·68 (s, 18-H), 0·84 (s, 19-H), 0·86 (d, J = 6 Hz, 26-H and 27-H), 0·90 (d, J = 6 Hz, 21-H), 1·97 (s, 7β-acetate), 5·00 (broad mt, 7α-H). For $C_{30}H_{50}O_2$ (442·7) calculated: 81·39% C, 11·38% H; found: 81·25% C, 11·40% H.

6α-Bromo-B-homo-5α-cholestan-7-one (*XXXIII*)

The ketone *XXIX* (350 mg) in glacial acetic acid (5 ml) was treated successively with 1 drop of 48% HBr, one drop of ethanol, and bromine (140 mg) in acetic acid (4 ml). After 2 h at room temperature the reaction mixture was poured into water (100 ml) and the product was extracted with ether. The ethereal solution was washed with 5% sodium hydrogen carbonate solution, water, dried, and evaporated. The residue (380 mg) was chromatographed over silica gel (10 g) in ligroin–ether (19 : 1). The corresponding fractions were combined, the solvent distilled off, and the residue was crystallised from methanol to yield 260 mg of the bromo ketone *XXXIII*, m.p. 61—64°C, $[\alpha]_D^{20}$ −21·6° (*c* 1·04); IR: 1709 cm^{-1}; NMR: 0·67 (s, 18-H), 0·72 (s, 19-H), 0·86 (d, J = 6 Hz, 26-H and 27-H), 0·88 (d, J = 6 Hz, 21-H), 2·39 (d, J = 11 Hz, 7aβ-H), 2·82 (t, J = 11 Hz, J' = 11 Hz, 7aα-H), 3·82 (d, J = 9 Hz, 6β-H). For $C_{28}H_{47}BrO$ (479·6) calculated: 70·12% C, 9·88% H, 16·66% Br; found: 70·41% C, 9·89% H, 16·90% Br.

7-Oxo-B-homo-5-cholestene (*XXXIV*)

a) The bromo ketone *XXXIII* (175 mg) in dimethylformamide (4 ml) was heated with lithium carbonate (175 mg) and lithium bromide (175 mg) to 120°C for 20 h. The reaction mixture was poured into water, the product taken into ether, the ethereal solution was washed with water, dried, and evaporated. The residue (150 mg) was chromatographed on a silica gel column (15 g) in ligroin–ether (49 : 1). The corresponding fractions were combined, evaporated, and the residue (113 mg) was crystallised from methanol to yield 89 mg of the unsaturated ketone *XXXIV*, m.p. 120—122°C, $[\alpha]_D^{20}$ −189·6° (*c* 1·32); IR: 1678, 1614 cm^{-1}; UV λ_{max}247 (log ε 3·86); NMR: 0·69 (s, 18-H), 0·86 (d, J = 6 Hz, 26-H and 27-H), 0·88 (d, J = 6 Hz, 21-H), 1·21 (s, 19-H), 2·23 (mt, 8β-H or one of the 4-H), 2·32 (d, J = 12 Hz, 7aβ-H), 2·91 (dd, J = 9 Hz, J = 12 Hz, 7aα-H), 5·78 (s, 6-H). For $C_{28}H_{46}O$ (398·6) calculated: 84·35% C, 11·63% H; found: 84·66% C, 11·70% H. *b*) Elution of the chromatography after isolation of the ketone *XXXV* under *a*) with the same solvent mixture, working up of the corresponding fractions, and crystallisation from methanol gave 180 mg of the ketone *XXXIV*, m.p. 120—122°C, $[\alpha]_D^{20}$ −190° (*c* 1·12).

7-Oxo-B-homo-4-cholestene (*XXXV*)

a) The bromoketone *XXXIII* (500 mg) in dimethylformamide (12 ml) was heated with lithium carbonate (500 mg) and lithium bromide (500 mg) to 140°C for 16 h. The reaction mixture was worked up as given in the foregoing experiment under *a*) and the residue was chromatographed on a silica gel column (50 g) in ligroin–ether (49 : 1). Fractions containing the more lipophilic unsaturated ketone were combined, and evaporated to yield 65 mg of the ketone *XXXV*, $[\alpha]_D^{20}$ +15·0° (*c* 1·62) which resisted all attempts at crystallisation; IR: 3020, 1705 cm^{-1}; NMR: 0·67 (s, 18-H), 0·85 (d, J = 6 Hz, 26-H and 27-H), 0·87 (s, 19-H), 0·89 (d, J = 6 Hz, 21-H), 2·60—3·00 (mt, 7a-H), 2·80 and 3·26 (2d, J = 18 Hz, 6-H), 5·47 (broad t, 4-H). For $C_{28}H_{46}O$ (398·6) calculated: 84·35% C, 11·63% H; found: 84·35% C, 11·71% H. *b*) The unsaturated ketone *XXXIV* (200 mg) in dimethylformamide (5 ml) was heated with lithium carbonate (200 mg) and lithium bromide (200 mg) to 140°C for 16 h. The reaction mixture was worked up as given for the preparation of the ketone *XXXIV* under *a*), and the residue was chromatographed over silica

gel (20 g) in ligroin–ether (49 : 1). Working up of the corresponding fractions gave next to the starting ketone (115 mg) 49 mg of the ketone *XXXV*, $[\alpha]_D^{20}$ +13·7° (*c* 1·19). *c*) The ketone *XXXIV* (300 mg) was refluxed with a solution of potassium hydroxide (2 g) in methanol (100 ml) for 4 hours. Methanol was removed under reduced pressure, the product taken into ether, and worked up. The residue was chromatographed preparatively on 6 silica gel plates (20 × 20 cm) in ligroin–ether (19 : 1). The corresponding zones were collected and eluted with ether. Next to the starting ketone (160 mg) 130 mg of the ketone *XXXV* were obtained, $[\alpha]_D^{20}$ +16·2° (*c* 1·16). *d*) The alcohol *XXXVI* (30 mg) in acetone (5 ml) was treated with excess Jones'reagent and allowed to stand at room temperature for 5 min. The excess oxidising agent was removed with methanol, the reaction mixture was poured into water, and the product was isolated with ether. The ethereal solution was washed with a sodium hydrogen carbonate solution, water, dried, and evaporated, to give 30 mg of the ketone *XXXV*, $[\alpha]_D^{20}$ +14·6° (*c* 1·17). *e*) The alcohol *XV* (50 mg) in acetone (5 ml) was oxidised with Jones'reagent as given in the foregoing experiment. Similar working up and evaporation of the solvent left 50 mg of a crude product which was chromatographed preparatively on 2 silica gel plates (20 × 20 cm) in ligroin–ether (9 : 1). Collection of the corresponding zones, elution with ether, and evaporation of the solvent gave 39 mg of the ketone *XXXV*, $[\alpha]_D^{20}$ +16·2° (*c* 1·34).

7α-Hydroxy-B-homo-4-cholestene (*XXXVI*)

a) The zones with the more polar component (preparation of the alcohol *XV* under *b*)) were collected, eluted with ether, and the solvent was evaporated. The residue (105 mg) was crystallised from ethanol–acetone–water to yield 40 mg of the alcohol *XXXVI*, m.p. 58–62°C, $[\alpha]_D^{20}$ −34·7° (*c* 0·84); IR: 3610, 3020, 1652, 1042, 1009 cm^{-1}; NMR: 0·66 (s, 18-H), 0·86 (d, J = = 6 Hz, 26-H and 27-H), 0·90 (d, J = 6 Hz, 21-H), 0·93 (s, 19-H), 2·34 (dd, J = 7 Hz, J = 15 Hz, 7aβ-H), 3·90 (broad mt, 7-H), 5·35 (broad t, 4-H). For $C_{28}H_{48}O$ (400·7) calculated: 83·93% C, 12·08% H; found: 84·01% C, 12·11% H. *b*) Elution of the chromatography after preparation of the alcohol *XV* under *c*) with ligroin–ether (19 : 1), combination of the corresponding fractions, evaporation of the solvent, and crystallisation from ethanol–acetone–water yielded 19 mg of the alcohol *XXXVI*, m.p. 58–61°C, $[\alpha]_D^{20}$ −36·2° (*c* 0·65).

The authors wish to express their sincere thanks to Academician F. Šorm for his continual interest and valuable advices. The analyses were carried out in the Analytical Laboratories of this Institute by Mr V. Štěrba, Mrs V. Rusová and Mrs E. Sýkorová under the direction of Dr J. Horáček. The infrared and ultraviolet spectra were recorded by Mrs K. Matoušková and by Mr P. Formánek under the direction od Dr J. Smolíková. The mass spectra were recorded by Dr L. Dolejš. The NMR spectra were recorded and interpreted by Dr P. Sedmera and Dr M. Buděšinský. Technical assistance was provided by Mrs J. Mašková.

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Translated by the author (J. F.).