ON STEROIDS. CLIX.* B-HOMOSTEROIDS. X.**

5,7-CYCLO-B-HOMOSTEROIDS SUBSTITUTED IN POSITIONS 2 AND 4

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The synthesis of the 2- and 4-oxo derivatives of the 5β,7β- as well as of the 5α,7α-cyclo-B-homocholestane series is described and their structures determined by chemical and spectral means.

In connection with our studies of the stereochemistry of 5,7-cyclo-B-homosteroids[1] we became interested in the 2- and 4-substituted compounds of this series. In this paper we describe the synthesis of the corresponding alcohols and ketones.

When the olefin *I* was oxidised with tert-butyl chromate in tetrachloromethane at the boiling point two products were obtained in a relation of about 2 : 1 in favour of the lower melting component. Both compounds proved to be α,β-unsaturated ketones, the lower melting one showed UV absorption at 222 nm, the higher melting one at 267 nm. Their structures were proved by unambiguous syntheses as follows: Simmons-Smith methylenation of 5-cholesten-4α-ol (*V*) afforded the alcohol *VI* which on oxidation yielded the ketone *III*, identical with the ketone obtained from the lower melting product on hydrogenation. This product is therefore the 4-oxo derivative *II*.

To prove the structure of the higher melting product the olefin *I* was transformed by hypobromous acid addition into a mixture of two bromohydrins. When dehalogenated, one of them gave the known[2] 3β-hydroxy derivative *X*, the other a new alcohol, evidently the 2β-hydroxy derivative *VIII* as follows from the fact that both bromohydrins gave the same epoxide on alkali treatment. This must be the 2β,3β-epoxide *XII* and the bromohydrins have structures *IX* and *XI*. The final structural proof of the higher melting tert-butyl chromate oxidation product is given by its hydrogenation to the same ketone *VII* which was also obtained by oxidation of the 2β-hydroxy derivative *VIII*. This higher melting product is therefore the 2-oxo derivative *IV*. The NMR spectra are in agreement with these structures: Whereas in the ketone *II* one olefinic proton appeared as a doublet (6·02 p.p.m.) and one as an octet

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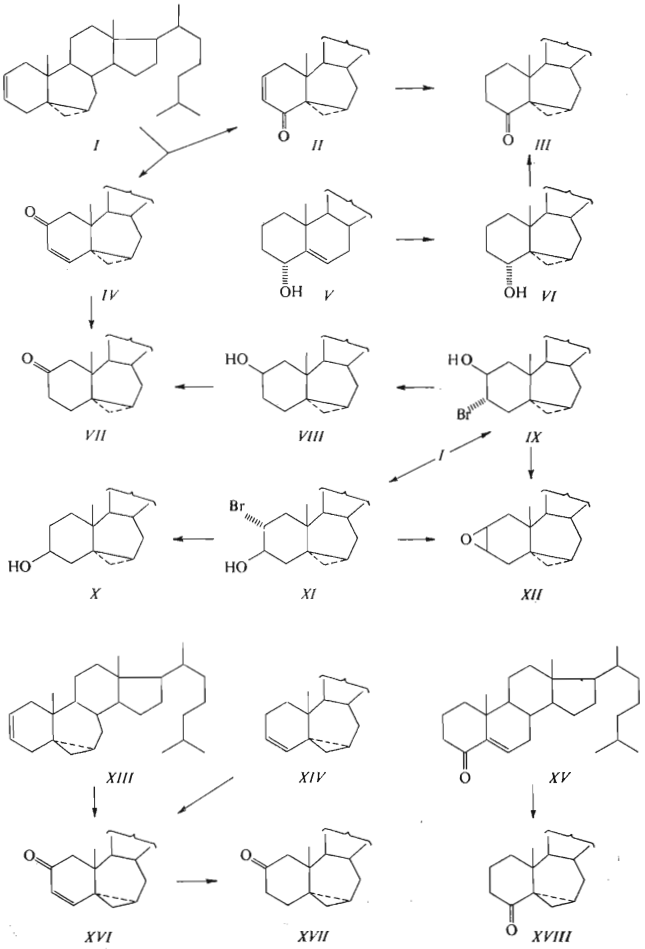
I
II
III
IV
V
VI
VII
VIII
IX
X
XI
XII
XIII
XIV
XV
XVI
XVII
XVIII

(6·80 p.p.m.), the analogous protons in the ketone *IV* appeared as two doublets centered at 5·98 p.p.m. and at 6·27 p.p.m., respectively.

In the 5α,7α-cyclo series the olefin *XIII* afforded on tert-butyl chromate oxidation only one unsaturated ketone with a UV absorption at 265 nm. In the NMR spectrum the olefinic protons appeared as two doublets centered at 5·76 p.p.m. and at 5·89 p.p.m. This points to the structure *XVI*. This structure was also proved by synthesis from the olefin *XIV* by tert-butyl chromate oxidation. Hydrogenation afforded the saturated 2-oxo compound *XVII*. The 4-oxo derivative *XVIII* was obtained from the unsaturated ketone *XV* on reaction with diazomethane in 20% yield[3].

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 CD spectra were recorded on the Roussel–Jouan spectrometer. The infrared spectra were recorded on the Zeiss UR 10 spectrometer in tetrachloromethane unless otherwise stated. UV spectra were recorded on the CF4 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 (compound *VII* and *VIII* on the Tesla 80 MHz-instrument) in deuteriochloroform with tetramethylsilane as internal reference unless otherwise stated. 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, 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, and water, drying with magnesium sulphate, and evaporation of the solvent.

5,7β-Cyclo-B-homo-5β-cholest-2-en-4-one (*II*)

A solution of the olefin *I* (1·2 g) in tetrachloromethane (12 ml) was heated to the boiling point and treated under stirring with tert-butyl chromate (7·9 ml), acetic acid (2·49 ml), and acetic anhydride (0·99 ml). After stirring at the boiling temperature for 6 h the reaction mixture was cooled off and treated with a solution of oxalic acid (1760 mg) in water (3·3 ml) and then with oxalic acid (1210 mg). After stirring at room temperature for 2 h the reaction mixture was treated with water, and tetrachloromethane, the organic layer was separated, washed with 5% sodium hydrogen carbonate solution, water, dried, and evaporated. The oily residue (990 mg) was chromatographed on a silica gel column (200 g) in ligroin–ether (33 : 1). Fractions with the lipophilic component were combined, evaporated, and the residue (480 mg) was crystallised from methanol to yield 380 mg of the ketone *II*, m.p. 115–117°C, $[\alpha]_D^{20}$ −49·6° (*c* 0·81). IR: 3055, 3025, 1678, 1640, 1619 cm^{-1}. UV: λ_{max} 222 nm (log ε 3·92). CD: Δε −0·72 (323 nm), −4·93 (249 nm). NMR: 0·64 (s, 18-H); 0·88 (d, J = 6 Hz, 26-H and 27-H); 0·91 (d, J = 6 Hz, 21-H); 1·15 (s, 19-H); 6·02 (d with fine splitting, $J_{3,2}$ = 10 Hz, $J_{3,1}$ = 2·5 + 1·5 Hz, 3-H); 6·80 (octet, $J_{2,3}$ = 10 Hz, $J_{2,1}$ = 5·5 + 3·0 Hz, 2-H). For $C_{28}H_{44}O$ (396·6) calculated: 84·77% C, 11·18% H; found 84·40% C, 11·33% H.

5,7β-Cyclo-B-homo-5β-cholestan-4-one (*III*)

a) *From* 5,7β-*cyclo*-B-*homo*-5β-*cholest*-2-*en*-4-*one* (II): The unsaturated ketone *II* (80 mg) in ethanol (3 ml) and ethyl acetate (3 ml) was hydrogenated over 5% $Pd/CaCO_3$ catalyst (100 mg) for 2 h. The catalyst was filtered off, washed with ether, the solvent was evaporated, and the residue (80 mg) was chromatographed preparatively on two plates of silica gel (20 × 20 cm) in ligroin–ether (9 : 1). The corresponding zones were collected, the product eluted with ether, and the solvent was removed. The residue was crystallised from methanol to yield 54 mg of the ketone *III*, m.p. 119–121°C, $[\alpha]_D^{20}$ −95° (*c* 0·51). IR: 3063, 1706 cm^{-1}. UV: λ_{max} 212 nm, log ε 3·19. NMR: 0·32 (mt, one cyclopropane proton); 0·60 (s, 18-H); 0·84 (d, *J* = 6 Hz, 26-H and 27-H); 0·87 (d, *J* = 6 Hz, 21-H); 1·00 (s, 19-H). For $C_{28}H_{46}O$ (398·6) calculated: 84·35% C, 11·63% H; found: 84·32% C, 11·52% H.

b) *From* 5,7β-*cyclo*-B-*homo*-5β-*cholestan*-4α-*ol* (VI): The alcohol *VI* (800 mg) in acetone (80 ml) was treated with excess Jones' reagent. After 5 minutes at room temperature the excess agent was removed with methanol, the reaction mixture diluted with water, and the product taken into ether. The ethereal solution was washed with 5% sodium hydrogen carbonate solution, water, dried, and evaporated. The residue was chromatographed on a silica gel column (20 g) in ligroin-ether (19 : 1). The corresponding fractions were combined, evaporated, and the residue was crystallised from methanol to yield 530 mg of the ketone *III*, m.p. 118–120°C, $[\alpha]_D^{20}$ −90° (*c* 1·69).

5,7β-Cyclo-B-homo-5β-cholest-3-en-2-one (*IV*)

Elution of the chromatography after isolation of the ketone *II* with the same solvent mixture afforded fractions with the polar component. Working up gave 225 mg of a product which on crystallisation from methanol yielded 165 mg of the ketone *IV*, m.p. 133–134°C, $[\alpha]_D^{20}$ −192° (*c* 0·64). IR: 3055, 3015, 1678, 1607 cm^{-1}. UV: λ_{max} 267 nm, log ε 3·83. CD: $\Delta\varepsilon = +1{\cdot}12$ (314·5 nm), −9·54 (264 nm). NMR: 0·64 (s, 18-H); 0·86 (d, *J* = 6 Hz, 26-H and 27-H); 0·90 (d, *J* = 6 Hz, 21-H); 1·16 (s, 19-H); 5·98 (d, *J* = 9 Hz, one olefinic proton); 6·27 (d, *J* = 9 Hz, one olefinic proton). For $C_{28}H_{44}O$ (396·6) calculated: 84·77% C, 11·18% H; found: 84·93% C, 11·26% H.

5,7β-Cyclo-B-homo-5β-cholestan-4α-ol (*VI*)

0·7% Zn—Cu couple was prepared by adding zinc dust (10·4 g) into a solution of cupric acetate monohydrate (240 mg) in acetic acid (10 ml) at 50–60°C and shaking until the solution decolorised. Fresh acetic acid (10 ml) was added and the sedimented zinc was decanted with eight portions (10 ml each) of ether. The couple was then covered with ether (40 ml), diiodomethane (9·2 ml) and one crystal of iodine were added and the mixture refluxed for 2 h in a nitrogen atmosphere. The mixture was then treated with a solution of the olefin *V* (3 g) in ether (40 ml) and refluxed for additional 2 h under nitrogen. After cooling off the reaction mixture was decomposed by pouring it into a sodium hydrogen carbonate solution (7%; 200 ml) and the product was extracted with ether. The ethereal solution was washed with 5% hydrochloric acid, a sodium hydrogen carbonate solution, water, a saturated sodium thiosulphate solution, water, dried, and evaporated. The residue (3 g) was dissolved in ether (50 ml), treated with a solution of perphthalic acid (3 g) in ether (22 ml) and allowed to stand at room temperature for 20 h. The reaction mixture was diluted with ether, the excess peracid was removed with 5% sodium carbonate solution and the ethereal solution was washed with water, dried, and evaporated. The residue

(3·2 g) was chromatographed over silica gel (250 g) in ligroin–ether (4 : 1). The corresponding fractions were combined, evaporated, and the residue (1·52 g) was crystallised from acetone to afford 1·36 g of the alcohol *VI*, m.p. 143–146°C, $[\alpha]_D^{20}$ −50·3° (*c* 1·27). IR: 3630, 3380, 3073 cm^{-1}. NMR: 0·16 (t, one cyclopropane proton); 0·46 (dd, one cyclopropane proton); 0·60 (s, 18-H); 0·84 (d, J = 6 Hz, 26-H and 27-H); 0·87 (d, J = 6 Hz, 21-H); 1·04 (s, 19-H); 4·01 (broad d, $J_{4\beta,3\alpha}$ = 11 Hz, $J_{4\beta,3\beta} \leqq$ 5 Hz). For $C_{28}H_{48}O$ (400·7) calculated: 83·93% C, 12·08% H; found: 84·09% C, 12·15% H.

5,7β-Cyclo-B-homo-5β-cholestan-2-one (*VII*)

a) *From* 5,7β-*cyclo*-B-*homo*-5β-*cholest*-3-*en*-2-*one* (IV): The unsaturated ketone *IV* (42 mg) in ethanol (4 ml) and ethyl acetate (4 ml) was hydrogenated over 5% $Pd/CaCO_3$ catalyst (50 mg) for 4 hours at room temperature. The catalyst was filtered off, washed with ether, and the solvents distilled off. The residue was crystallised from methanol to yield 21 mg of the ketone *VII*, m.p. 136–139°C, $[\alpha]_D^{20}$ −35·7° (*c* 0·45). IR: 3055, 1710 cm^{-1}. NMR: 0·66 (s, 18-H); 0·85 (d, J = = 6 Hz, 26-H and 27-H); 0·88 (d, J = 5·6 Hz, 21-H); 1·00 (s, 19-H); 2·35 (d, two protons, 1-H or 3-H). For $C_{28}H_{46}O$ (398·6) calculated: 84·35% C, 11·63% H; found: 84·37% C, 11·70% H.

b) *From* 5,7β-*cyclo*-B-*homo*-5β-*cholestan*-2β-*ol* (VIII): A solution of the alcohol *VIII* (50 mg) in acetone (5 ml) was treated with excess Jones'reagent and allowed to stand 5 minutes at room temperature. The excess oxidising agent was removed with methanol, the reaction mixture was diluted with water, and the product was taken into ether. The ethereal layer was washed with water, a sodium hydrogen carbonate solution, water, dried, and the solvent was distilled off. The residue (48 mg) was crystallised from methanol to yield 27 mg of the ketone *VII*, m.p. 138 to 140°C, $[\alpha]_D^{20}$ −38·6° (*c* 1·02).

5,7β-Cyclo-B-homo-5β-cholestan-2β-ol (*VIII*)

The bromohydrin *IX* (100 mg) in ethanol (5 ml) and ethyl acetate (5 ml) was dehalogenated over 5% $Pd/CaCO_3$ catalyst in a hydrogen atmosphere for 24 h at room temperature. The catalyst was filtered off, washed with ether and solvents removed under reduced pressure. The residue was chromatographed preparatively on two plates of silica gel (20 × 20 cm) in ligroin–ether (2 : 1). The corresponding zones were collected, product eluted with ether, and worked up. The amorphous product which separated from the ligroin solution was collected by suction. Yield 65 mg of the alcohol *VIII*, m.p. 140–142°C, $[\alpha]_D^{20}$ −58° (*c* 0·74). IR: 3620, 3055 cm^{-1}. NMR: 0·09 and 0·31 (two mt, two cyclopropane protons); 0·60 (s, 18-H); 0·85 (d, J = 6 Hz, 26-H and 27-H); 0·88 (d, J = 5·6 Hz, 21-H); 1·32 (s, 19-H); 3·05 (mt, W = 15 Hz, 2α-H). For $C_{28}H_{48}O$ (400·7) calculated: 83·93% C, 12·08% H; found: 84·11% C, 12·11% H.

3α-Bromo-5,7β-cyclo-B-homo-5β-cholestan-2β-ol (*IX*)

A solution of the olefin *I* (940 mg) in dioxane (150 ml) and water (3 ml) was treated with 0·9% perchloric acid (2·2 ml) and N-bromoacetamide (400 mg). After 2 hours at room temperature the reaction mixture was diluted with water (100 ml), the product extracted into ether, and the ethereal solution was washed with sodium hydrogen carbonate solution, water, dried, and ether distilled off. The residue (1·1 g) was chromatographed over silica gel (100 g) in ligroin–ether (9 : 1). Fractions containing the lipophilic bromohydrin were combined, evaporated, and the residue was crystallised from methanol to afford 550 mg of the bromohydrin *IX*, m.p. 143–145°C $[\alpha]_D^{20}$ −6·9° (*c* 1·15). IR: 3610, 3065 cm^{-1}. NMR (chloroform): 0·60 (s, 18-H); 0·84 (d, J = 6 Hz,

26-H and 27-H); 0·87 (d, $J = 6$ Hz, 21-H); 1·20 (s, 19-H); 2·90 (broad dd, $J = 15$ Hz, $J' = 5$ Hz, 3β-H); 4·35 (broad t, $W = 8$ Hz, 2α-H). For $C_{28}H_{47}BrO$ (479·6) calculated: 70·12% C, 9·88% H, 16·66% Br; found: 70·39% C, 9·92% H, 16·57% B.

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

The bromohydrin *XI* (180 mg) in ethanol (5 ml) and ethyl acetate (5 ml) was dehalogenated over 5% $Pd/CaCO_3$ catalyst (200 mg) under the presence of ammonium acetate (180 mg) in a hydrogen atmosphere for 4 h at room temperature. Catalyst was filtered off, washed with ether, the filtrate was washed with water, dried, and evaporated. The residue was chromatographed preparatively on three plates of silica gel (20 × 20 cm) in ligroin–ether (3 : 1). The corresponding zones were collected, the product eluted with ether, and the solvent was distilled off. The residue (135 mg) was crystallised from acetone to afford 80 mg of the alcohol *X*, m.p. 157—158°C, $[\alpha]_D^{20}$ −44·9° (*c* 1·19), identical with the authentic sample[2].

2α-Bromo-5,7β-cyclo-B-homo-5β-cholestan-3β-ol (*XI*)

Elution of the column after isolation of the bromohydrin *IX* with the same solvent mixture afforded fractions with the polar isomer. Working up and evaporation of the solvent gave 27 mg of a product which on crystallisation from methanol yielded 15 mg of the bromohydrin *XI*, m.p. 55—58°C, $[\alpha]_D^{20}$ −34·3° (*c* 1·14). IR: 3570, 3060 cm^{-1}. NMR: 0·05—0·50 (mt, two cyclopropane protons); 0·58 (s, 18-H); 0·83 (d, $J = 6$ Hz, 26-H and 27-H); 0·86 (d, $J = 6$ Hz, 21-H); 1·08 (s, 19-H); 3·72 (mt, 3α-H); 4·32 (mt, 2β-H). For $C_{28}H_{47}BrO$ (479·6) calculated: 70·12% C, 9·88% H, 16·66% Br; found: 70·40% C, 9·81% H, 16·70% Br.

2β,3β-Epoxy-5,7β-cyclo-B-homo-5β-cholestane (*XII*)

a) *From* 3α-*bromo*-5,7β-*cyclo*-B-*homo*-5β-*cholestan*-2β-*ol* (IX): The bromohydrin *IX* (120 mg) in methanol (30 ml) was refluxed with potassium hydroxide (240 mg) for 30 minutes. The reaction mixture was diluted with water, the product extracted with ether, and the ethereal solution worked up as usual. The residue (102 mg) was crystallised from ethanol to yield 75 mg of the epoxide *XII*, m.p. 108—110°C, $[\alpha]_D^{20}$ −24·0° (*c* 1·66). IR: 3 060 cm^{-1}. NMR: 0·10—0·30 (mt, two cyclopropane protons); 0·57 (s, 18-H); 0·83 (d, $J = 6$ Hz, 26-H and 27-H); 0·87 (d, $J = 6$ Hz, 21-H); 1·10 (s, 19-H); 3·19 (mt, 2α-H and 3α-H). For $C_{28}H_{46}O$ (398·6) calculated: 84·35% C, 11·63% H; found: 84·34% C, 11·53% H,

b) *From* 2α-*bromo*-5,7β-*cyclo*-B-*homo*-5β-*cholestan*-3β-*ol* (XI): The bromohydrin *XI* (60 mg) in methanol (20 ml) was refluxed with potassium hydroxide (120 mg) for 30 minutes. Similar working up as given in the previous experiment afforded a crude product which was purified by preparative thin-layer chromatography on two plates of silica gel (20 × 20 cm) in ligroin–ether (9 : 1). The corresponding zones were collected, eluted with ether, and the residue after evaporation of the solvent was crystallised from methanol to yield 23 mg of the epoxide *XII*, m.p. 105—108°C, $[\alpha]_D^{20}$ −23·3° (*c* 1·46).

5,7α-Cyclo-B-homo-5α-cholest-3-en-2-one (*XVI*)

a) *From* 5,7α-*cyclo*-B-*homo*-5α-*cholest*-2-*ene* (XIII): A solution of the olefin *XIII* (330 mg) in tetrachloromethane (5 ml) was treated with tert-butyl chromate (2·4 ml), acetic acid (0·8 ml) and acetic anhydride (0·3 ml) as described for the preparation of the ketone *II*. Similar working

up afforded a residue (350 mg) which was chromatographed over silica gel (50 g) in ligroin–ether (33 : 1). Working up of the corresponding fractions afforded next to the starting olefin (105 mg) 95 mg of the product which on crystallisation from methanol yielded 56 mg of the ketone *XVI*, m.p. 108–110°C, $[\alpha]_D^{20}$ +67° (*c* 0·63). IR: 3085, 1682, 1613 cm^{-1}. UV λ_{max} 265 nm (log ε 3·97). NMR: 0·62 (mt, one cyclopropane proton); 0·63 (s, 18-H); 0·84 (d, J = 6 Hz, 26-H and 27-H); 0·88 (d, J = 6 Hz, 21-H); 0·92 (s, 19-H); 2·31 (d, J_{gem} = 15 Hz, one 1-H); 2·58 (d, J_{gem} = 15 Hz, one 1-H); 5·76 (d, $J_{3,4}$ = 10 Hz, 3-H or 4-H), 5·89 (d, $J_{3,4}$ = 10 Hz, 3-H or 4-H). For $C_{28}H_{44}O$ (396·6) calculated: 84·77% C, 11·18% H; found: 84·67% C, 11·27% H.

b) *From* 5,7α-*cyclo*-B-*homo*-5α-*cholest*-3-*ene* (XIV): The olefin *XIV* (500 mg) in tetrachloromethane (5 ml) was heated to boiling temperature and treated under stirring with tert-butyl chromate (3·6 ml), acetic acid (1·13 ml) and acetic anhydride (0·45 ml). The reaction mixture was stirred at the same temperature for 40 minutes and then decomposed as described for the preparation of the ketone *II*. Similar working up gave a product (450 mg) which was chromatographed over silica gel (50 g) in ligroin–ether (33 : 1). Working up of the corresponding fractions afforded 110 mg of a product which on crystallisation from methanol gave 82 mg of the ketone *XVI*, m.p. 115–117°C, recrystallisation at 109–110°C, $[\alpha]_D^{20}$ +65·7° (*c* 0·48).

5,7α-Cyclo-B-homo-5α-cholestan-2-one (*XVII*)

The ketone *XVI* (47 mg) in ethanol (3 ml) and ethyl acetate (3 ml) was hydrogenated over 5% $Pd/CaCO_3$ catalyst (90 mg) for 2 h at room temperature. The catalyst was filtered off, washed with ether and the filtrate was evaporated. The residue was purified by preparative thin-layer chromatography on two plates of silica gel (20 × 20 cm) in ligroin–ether (9 : 1). The corresponding zones were collected, the product eluted with methanol, the residue after evaporation of methanol was dissolved in chloroform, the solution was filtered, chloroform removed by distillation, and the residue was crystallised from methanol. Yield 24 mg of the ketone *XVII*, m.p. 83–85°C, $[\alpha]_D^{20}$ −47·6° (*c* 0·81). IR: 3065, 1717 cm^{-1}. NMR (chloroform): 0·33 (mt, two cyclopropane protons); 0·59 (s, 18-H); 0·84 (d, J = 6 Hz, 26-H and 27-H); 0·86 (d, J = 6 Hz, 21-H); 0·93 (s, 19-H). For $C_{28}H_{46}O$ (398·6) calculated: 84·35% C, 11·63% H; found: 84·32% C, 11·57% H.

5,7α-Cyclo-B-homo-5α-cholestan-4-one (*XVIII*)

The unsaturated ketone *XV* (20 g) was dried by azeotropic distillation with benzene (200 ml), the residue was dissolved in ether (1 600 ml) and treated with a solution of diazomethane (8·4 g) in ether (300 ml). Small portions of aluminium chloride (about 50 mg each) were added to keep the reaction in moderate progress for 30 minutes. The reaction mixture was then allowed to stand for 15 minutes, diluted with water, and the product extracted into ether. The ethereal solution was worked up, and the residue (20 g) was chromafographed on a silica gel column (2 kg) in ligroin–ether (33 : 1). Working up of the corresponding fractions afforded 4·7 g of a product which on crystallisation from methanol gave 3·6 g of the ketone *XVIII*, m.p. 104–106°C, $[\alpha]_D^{20}$ +49·4° (*c* 1·45). IR: 3085, 3005, 1680 cm^{-1}. UV: λ_{max} 215 nm (log ε 3·59). NMR (chloroform): 0·63 (18-H); 0·85 (d, J = 6 Hz, 26-H and 27-H); 0·88 (d, J = 6 Hz, 21-H); 0·94 (s, 19-H); 2·32 (broad mt, 3-H). For $C_{28}H_{46}O$ (398·6) calculated: 84·35% C, 11·63% C, 11·63% H; found: 84·15% C, 11·74% H.

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REFERENCES

1. Kohout L., Fajkoš J.: This Journal *38*, 913 (1973).
2. Kohout L., Fajkoš J.: This *37*, 3490 (1972).
3. Velgová H.: Unpublished results.

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