PREPARATION OF SOME 5-HYDROXY-5α-CHOLEST-2-ENES*

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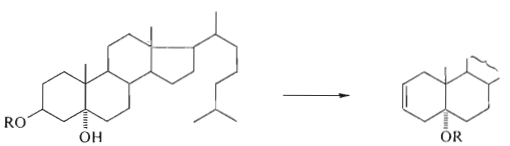
Improved syntheses of 5-hydroxy-5α-cholest-2-enes *III*, *IX*, *XVIII*, *XXII* and *XXIX* from corresponding 3β-tosyloxy- and 3β-mesyloxy compounds are described.

In connection with another investigation, we needed a series of 5-hydroxy-5α-cholest--2-enes including the compounds *III*, *IX*, *XVIII*, *XXII* and *XXIX*. Except for *IX*, these substances are known. However, since we were able to find shorter routes or procedures furnishing higher yields, we are presenting these results in this paper.

In the preparation of 5-hydroxy-5α-cholest-2-ene[1,2] (*III*) we started from the diol[3,4] *I via* the mesylate[5] *II*. The latter compound could be contained in purer condition than reported[5] and was converted to *III* by treatment with boiling collidine.



I, R = H
II, R = Mes

III, R = H
IV, R = Ac

Two parallel routes starting from cholesteryl tosylate (*V*) and cholesteryl benzoate (*VI*), respectively, were chosen for the synthesis of the 6-oxo compound[6] *XVIII*. Monoperphthalic acid oxidation of *V* or *VI* gave mixtures of epimeric epoxides[7] *X* or *XI* (ref.[8]) which were converted to hydroxy ketones *XII* (ref.[6,10]) or *XIV* (ref.[11]) by oxidation with chromium trioxide using a method applied previously[9] to a similar case in androstane series. The two compounds were characterized as 5-acetates *XIII*[10] and *XV*. The benzoate *XIV* was converted to mesylate *XVII via* the known[10] alcohol *XVI*. The 2-unsaturated compound[6] *XVIII* was prepared from the tosylate *XII* and mesylate *XVII* by refluxing with collidine which proved to be superior

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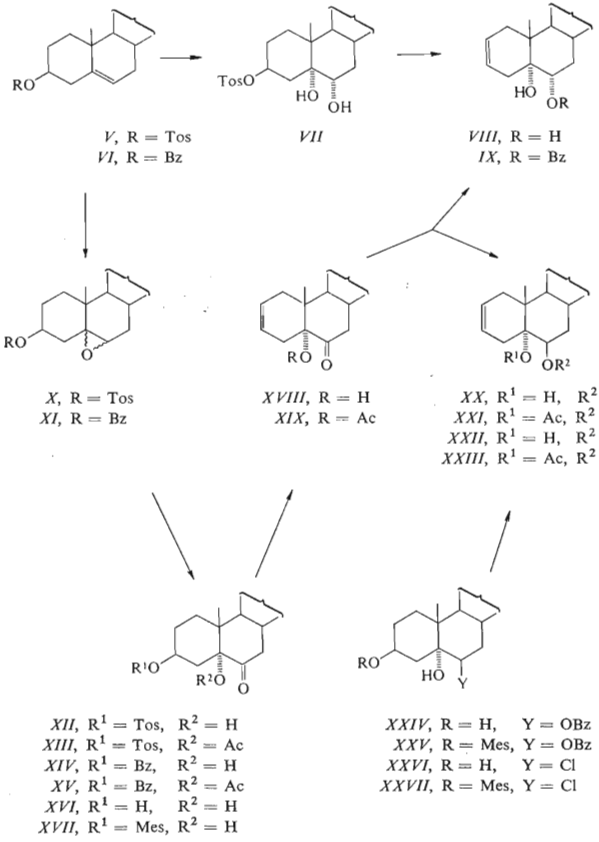
to pyridine[6]. Similarly, the 6-benzoyloxy derivative[12] *XXII* was prepared from the alcohol[8] *XXIV via* the mesylate *XXV*.



V, R = Tos
VI, R = Bz

VII

VIII, R = H
IX, R = Bz

X, R = Tos
XI, R = Bz

XVIII, R = H
XIX, R = Ac

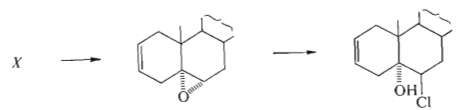
XX, R^1 = H, R^2 = H
XXI, R^1 = Ac, R^2 = H
XXII, R^1 = H, R^2 = Bz
XXIII, R^1 = Ac, R^2 = Bz

XII, R^1 = Tos, R^2 = H
XIII, R^1 = Tos, R^2 = Ac
XIV, R^1 = Bz, R^2 = H
XV, R^1 = Bz, R^2 = Ac
XVI, R^1 = H, R^2 = H
XVII, R^1 = Mes, R^2 = H

XXIV, R = H, Y = OBz
XXV, R = Mes, Y = OBz
XXVI, R = H, Y = Cl
XXVII, R = Mes, Y = Cl

For the preparation of the 5α,6α-diol *VIII*, osmium tetroxide hydroxylation of the double bond in the tosylate *V* followed by collidine treatment proved to be a very

suitable method. However, for large scale preparation reduction of the 6-oxo group in 5α-hydroxy- or 5α-acetoxy-6-oxo-derivatives *XVIII* and *XIX* was investigated. Sodium borohydride reduction proved unfeasible since both *XVIII* and *XIX* yielded 6β-hydroxy derivatives *XX* and *XXI*, respectively. The same results was achieved by lithium aluminum hydride reduction of the hydroxy ketone *XVIII*. More successful was lithium aluminum hydride reduction of the acetate *XIX* where the 6α-hydroxy derivative *VIII* was formed along with the 6β-alcohol *XX*. In spite of the unfavorable proportion (1 : 2) of both products, the method is suitable for preparative purposes since the products can be easily separated by chromatography. The desired benzoyloxy derivative *IX* was prepared from *VIII*.



XXVIII *XXIX*

The compound[12] *XXIX* was prepared from the 5α,6α-epoxy tosylate *X* by the collidine method to yield the olefin *XXVIII* and cleavage of the epoxide ring in the latter compound with hydrochloric acid. A pathway *via* the mesylate *XXVII* proved unfeasible since collidine treatment of the latter compound led to a complex mixture.

EXPERIMENTAL

Melting points were determined on a Kofler block. Analytical samples were dried at 50°C/0·2 Torr. Optical measurements were carried out in chloroform with an error of ±1°. The infrared spectra were recorded on a Zeiss UR 20 spectrometer in tetrachloromethane unless otherwise stated. The ^{1}H-NMR spectra were recorded on a Varian HA-100 instrument in deuteriochloroform with tetramethylsilane as internal reference at 30°C. Chemical shifts are given in ppm. Apparent coupling constants were obtained from the first order analysis. The mass spectra were recorded on a AEI MS 907 mass spectrometer. The CD spectra were recorded on a Dichrographe II (Jouan-Roussel) in methanol. The identity of samples prepared by different routes was checked by mixture melting point determination, by thin-layer chromatography (TLC) and by infrared and ^{1}H-NMR spectra. Usual work up of an ethereal solution means washing the solution with 5% aqueous hydrochloric acid, water, 5% aqueous potassium hydrogen carbonate solution, water, drying with sodium sulfate and evaporation of the solvent *in vacuo*.

5α-Cholestane-3β,5-diol 3-Monomethanesulfonate (*II*)

A solution of alcohol[3,4] *I* (5 g) in pyridine (30 ml) was treated at 0°C with methanesulfonyl chloride (4 ml) and allowed to stand at room temperature for 1 h. The mixture was decomposed with ice, diluted with water, the product taken up in ether and the ethereal solution was worked up as usual. The residue was crystallized from a mixture of acetone, methanol and water to yield

the mesylate *II* (4·6 g), m.p. 118—119° (literature reports[5] 110°C), $[\alpha]_D^{20}$ +22° (*c* 2·0). IR spectrum: 1179, 1368, 3540, 3610 cm^{-1}. ^{1}H-NMR spectrum: 0·67 (3 H, s, 18-H), 1·01 (3 H, s, 19-H), 2·98 (3 H, s, CH_3SO_3—), 5·0 (1 H, m, 3α-H). For $C_{28}H_{50}O_4S$ (482·8) calculated: 69·66% C, 10·44% H, 6·64% S; found: 69·50% C, 10·48% H, 6·49% S.

5α-Cholest-2-en-5-ol (*III*)

The mesylate *II* (4·5 g) in *sym*-collidine (15 ml) was refluxed under nitrogen for 1 h. Collidine was then distilled off under reduced pressure, the residue was diluted with water and 5% aqueous hydrochloric acid, and the product was extracted with ether. The ethereal solution was worked up as usual and the residue was crystallized from a mixture of acetone, methanol and water to afford the olefin *III* (3·1 g), m.p. 94—95°C, $[\alpha]_D^{20}$ +51° (*c* 2·0) in accordance with the literature[1,2]. IR spectrum 674, 1652, 3030, 3505, 3600 cm^{-1}. ^{1}H-NMR spectrum: 0·66 (3 H, s, 18-H), 0·88 (3 H, s, 19-H).

5α-Cholest-2-en-5-ol 5-Acetate (*IV*)

The alcohol *III* (250 mg) was dissolved in acetic acid (5 ml) and acetylated with acetic anhydride (1 ml) in the presence of *p*-toluenesulfonic acid (100 mg) at room temperature for 2 h. The mixture was decomposed with ice, the product was taken up in chloroform, the organic layer was washed with 5% aqueous potassium hydrogen carbonate solution, water, dried and the solvent evaporated to yield the noncrystalline acetate *IV* (235 mg), $[\alpha]_D^{20}$ −36° (*c* 1·9). ^{1}H-NMR spectrum: 0·68 (3 H, s, 18-H), 0·90 (3 H, s, 19-H), 1·97 (3 H, s, CH_3COO). For $C_{29}H_{48}O_2$ (428·7) calculated: 81·25% C, 11·29% H; found: 81·30% C, 11·31% H.

5α-Cholestane-3β,5,6α-triol 3-Monotoluenesulfonate (*VII*)

The tosylate *V* (2·1 g) was dissolved in pyridine (15 ml), treated with osmium tetroxide (1 g) and allowed to stand at room temperature overnight. The adduct was decomposed with a solution of sodium hydrogen sulfite (2 g) in water (30 ml) and pyridine (20 ml), the mixture was diluted with water, and the product taken up in ether. The ethereal solution was worked up as usual, and the residue was crystallized from a mixture of acetone, methanol and water to yield the diol *VII* (1·6 g), m.p. 152—153°C, $[\alpha]_D^{20}$ +18° (*c* 1·7). ^{1}H-NMR spectrum: 0·64 (3 H, s, 18-H), 0·94 (3 H, s, 19-H), 3·61 (1 H, m, 6β-H), 4·85 (1 H, m, 3α-H). For $C_{34}H_{54}O_5S$ (574·9) calculated: 71·04% C, 9·47% H, 5·58% S; found: 70·98% C, 9·45% H, 5·69% S.

5α-Cholest-2-ene-5,6α-diol (*VIII*)

a) *From 5α-cholestane-3β,5,6α-triol 3-monotoluenesulfonate*(VII): The tosylate *VII* (1 g) in *sym*-collidine (10 ml) was refluxed under nitrogen for 1 hour. The mixture was worked up as given for *III*. The residue was crystallized from a mixture of methanol and water to afford the olefin *VIII* (382 mg), m.p. 166—167°[3], $[\alpha]_D^{20}$ +50° (*c* 2·0). IR spectrum: 1658, 3585, 3602, 3630 cm^{-1}. ^{1}H-NMR spectrum: 0·67 (3 H, s, 18-H), 0·88 (3 H, s, 19-H), 3·60 (1 H, dd, 6β-H, $J_{6\beta,7\alpha}$ = 11 Hz, $J_{6\beta,7\beta}$ = 5 Hz). For $C_{27}H_{46}O_2$ (402·7) calculated: 80·54% C, 11·51% H; found: 80·67% C, 11·43% H.

b) *From 5-acetoxy-5α-cholest-2-en-6-one* (XIX): The ketone *XIX* (300 mg) was dissolved in ether (10 ml) and reduced with lithium aluminum hydride (100 mg) at room temperature for 1 h. The mixture was decomposed with saturated aqueous sodium sulfate solution, the pro-

duct extracted with ether and the ethereal solution worked up as usual. The residue was chromatographed on three preparative silica gel plates (20 × 20 cm) using double development with a mixture of benzene and ether (90 : 10) as eluent. The faster-moving substance (red spot with sulfuric acid) was the 5α,6β-diol *XX* (174 mg). The slower one (violet detection) was the 5α,6α-diol *VIII* (93 mg), m.p. 167–168°C (methanol–water), $[\alpha]_D^{20}$ +52° (*c* 1·6).

5α-Cholest-2-ene-5,6α-diol 6-Monobenzoate (*IX*)

The diol *VIII* (300 mg) was benzoylated with benzoyl chloride (1 ml) in pyridine (5 ml) at room temperature overnight. The mixture was decomposed with ice, the product taken up in ether and worked up as usual. The residue was crystallized from a mixture of acetone, methanol and water to yield the benzoate *IX* (173 mg), m.p. 206–207°C, $[\alpha]_D^{20}$ +45° (*c* 1·7). ^{1}H-NMR spectrum: 0·70 (3 H, s, 18-H), 0·98 (3 H, s, 19-H), 5·25 (1 H, brd. m., 6β-H). For $C_{34}H_{50}O_3$ (506·8) calculated: 80·58% C, 9·94% H; found: 80·63% C, 9·90% H.

3β-Toluenesulfonyloxy-5-hydroxy-5α-cholestan-6-one (*XII*)

The mixture of epimeric epoxides *X* (150 g) (ref.[7]) was dissolved in aceton (1 500 ml) and the solution of chromium trioxide (100 g) in water (140 ml) was added over a period of 15 minutes at 30–50°C. The mixture was stirred for an additional 10 minutes, diluted with water (3 l) and the crude product collected by filtration under suction. Recrystallization from a mixture of acetone, methanol and water gave the pure ketone *XII* (106 g), m.p. 167–168°C (literature reports[6,10] 135–136°, or 161–163°), $[\alpha]_D^{20}$ −51° (*c* 2·0) (literature reports[6,10] $[\alpha]_D^{20}$ −48°). For $C_{34}H_{52}O_5S$ (572·9) calculated: 71·29% C, 9·15% H, 5·60% S; found: 71·12% C, 9·23% H, 5·47% S.

3β-Toluenesulfonyloxy-5-acetoxy-5α-cholestan-6-one (*XIII*)

The ketone *XII* (5 g) was acetylated with acetic anhydride (20 ml) in acetic acid (200 ml) in the presence of *p*-toluenesulfonic acid (1 g) at room temperature overnight. The mixture was worked up as given for *IV*. The residue was crystallized from a mixture of acetone, methanol and water to afford the acetate *XIII* (3·1 g), m.p. 153–154°C (literature reports[10] 146–147°C), $[\alpha]_D^{20}$ +4° (*c* 2·0) (literature reports[10] +3·6°). ^{1}H-NMR spectrum: 0·64 (3 H, s, 18-H), 0·82 (3 H, s, 19-H) IR spectrum: 860, 1 180, 1 233, 1 372, 1 727, 1 748 cm^{-1}; CD spectrum: $\Delta\varepsilon$ −1·91, 293 nm.

3β-Benzoyloxy-5-hydroxy-5α-cholestan-6-one (*XIV*)

The mixture of epoxides *XI* (30 g) was dissolved in a mixture of acetone (300 ml) and benzene (100 ml), and the solution of chromium trioxide (20 g) in water (25 ml) was added over a period of 10 minutes at 30–40°C. The mixture was worked up as given for *XII*. Crystallization from acetone–dioxane–ethanol–water gave the pure ketone *XIV* (21 g), m.p. 236–237°C (literature reports[11] 230–231°C), $[\alpha]_D^{20}$ −29° (*c* 1·9), (literature reports[11] $[\alpha]_D^{20}$ −26°). For $C_{34}H_{50}O_4$ (522·8) calculated: 78·12% C, 9·64% H; found: 78·20% C, 9·59% H.

3β-Benzoyloxy-5-acetoxy-5α-cholestan-6-one (*XV*)

The ketone *XIV* (500 mg) was acetylated with acetic anhydride (5 ml) in acetic acid (50 ml) in the presence of *p*-toluenesulfonic acid (100 mg) at room temperature overnight. The mixture was worked up as given for *IV*. The residue was crystallized from a mixture of acetone, methanol and water to yield the acetate *XV* (410 mg), m.p. 180–181°C, $[\alpha]_D^{20}$ +5° (*c* 1·9). IR spectrum:

1235, 1275, 1721, 1748 cm^{-1}. CD spectrum: $\Delta\varepsilon$ −2·36, 293 nm; ^{1}H-NMR spectrum: 0·66 (3 H, s, 18-H), 0·92 (3 H, s, 19-H), 2·20 (3 H, s, CH_3COO). For $C_{36}H_{52}O_5$ (564·8) calculated: 76·56% C 9·28% H; found: 76·69% C, 9·32% H.

3β,5-Dihydroxy-5α-cholestan-6-one (*XVI*)

A solution of the benzoate *XIV* (20 g) and potassium hydroxide (10 g) in methanol (1 l) was refluxed for 2 h. Water was added to the hot solution and the mixture was allowed to stand at room temperature overnight. The crystalline product was collected by filtration under suction, washed with water and air-dried to afford the pure diol *XVI* (14 g), m.p. 230—232°C, $[\alpha]_D^{20}$ −33° (*c* 2·0), in accordance with the literature[10].

3β-Methanesulfonyloxy-5-hydroxy-5α-cholestan-6-one (*XVII*)

A solution of the diol *XVI* (10 g) in pyridine (70 ml) was treated at 0°C with methanesulfonyl chloride (7 ml) and allowed to stand at room temperature for 1 hour. The mixture was worked up as given for *II*. The residue was crystallized from a mixture of acetone, methanol and water to yield the mesylate *XVII* (6·7 g), m.p. 147—148°C, $[\alpha]_D^{20}$ −43° (*c* 2·1). IR spectrum: 1178, 1360, 1695 sh, 1705, 1715, 3495, 3590 cm^{-1}. ^{1}H-NMR spectrum: 0·66 (3 H, s, 18-H), 0·83 (3 H, s, 19-H), 3·01 (3 H, s, CH_3SO_3—), 5·0 (1 H, m, 3α-H), For $C_{28}H_{48}O_5S$ (496·8) calculated: 67·70% C, 9·74% H, 5·45% S; found: 67·53% C, 9·70% H, 5·31% S.

5-Hydroxy-5α-cholest-2-en-6-one (*XVIII*)

The mesylate *XVII* (15 g) in *sym*-collidine (50 ml) was refluxed for 1 h under nitrogen. The mixture was worked up as given for *III*, and the residue was crystallized from a mixture of acetone, methanol and water to yield the olefin *XVIII* (11·5 g), m.p. 140—141°C, $[\alpha]_D^{20}$ −23° (*c* 2·0) in accordance with the literature[6]. ^{1}H-NMR spectrum: 0·67 (3 H, s, 18-H), 0·73 (3 H, s, 19-H).

5-Acetoxy-5α-cholest-2-en-6-one (*XIX*)

a) *From* 3β-*toluenesulfonyloxy*-5-*acetoxy*-5α-*cholestan*-6-*one* (XIII): The tosylate *XIII* (500 mg) in *sym*-collidine (5 ml) was refluxed under nitrogen for 1 h. The mixture was worked up as given for *III*, and the residue was crystallized from a mixture of acetone, methanol and water to yield the olefine *XIX* (283 mg), m.p. 121—124°C.

b) *From* 5-*hydroxy*-5α-*cholest*-2-*en*-6-*one* (XVIII): The ketone *XVIII* (3·5 g) in acetic acid acid (60 ml) was acetylated with acetic anhydride (10 ml) in the presence of *p*-toluenesulfonic acid (1 g) at room temperature for 2 h. The mixture was worked up as given for *IV*. The residue was crystallized from acetone–methanol–water to afford the substance *XIX* (1·6 g), m.p. 133 to 134°C, $[\alpha]_D^{20}$ −20° (*c* 2·1). IR spectrum: 1242, 1659, 1724, 1742, 3035 cm^{-1}. CD spectrum: $\Delta\varepsilon$ −2·98, 293 nm; ^{1}H-NMR spectrum: 0·66 (3 H, s, 18-H), 0·74 (3 H, s, 19-H), 2·07 (3 H, s, H_3COO). For $C_{29}H_{46}O_3$ (442·7) calculated: 78·68% C, 10·47% H; found: 78·64% C, 10·49% H.C

5α-Cholest-2-ene-5,6β-diol (*XX*)

a) *From* 5-*acetoxy*-5α-*cholest*-2-*en*-6-*one* (XIX): The crude diol *XX*, obtained above from *XIX* along with *VIII*, was crystallized from aqueous methanol to yield pure product, m.p. 133—134°C, $[\alpha]_D^{20}$ +23° (*c* 2·0) in accordance with the literature[12]. IR spectrum: 1652, 3603, 3634 cm^{-1}. ^{1}H-NMR spectrum: 0·70 (3 H, s, 18-H), 1·06 (3 H, s, 19-H), 3·64 (1 H, m, 6α-H).

b) *From 5α-cholest-2-ene-5,6β-diol 5-acetate* (XXI): The acetate *XXI* (100 mg) in ether (10 ml) was reduced with lithium aluminum hydride (50 mg) at room temperature overnight. The reaction mixture was decomposed with saturated aqueous sodium sulfate solution, the product was extracted with ether and the ethereal solution was worked up as usual. The residue was crystallized from aqueous methanol to yield the diol *XX*, (43 mg), m.p. 133–135°C.

5α-Cholest-2-ene-5,6β-diol 5-Acetate (*XXI*)

The ketone *XIX* (200 mg) in ethanol (30 ml) was reduced with sodium borohydride (100 mg) at room temperature overnight. The reaction mixture was decomposed with 5% aqueous hydrochloric acid, diluted with water and the product extracted with ether. The ethereal solution was worked up as usual and the residue chromatographed on two plates of silica gel (20 × 20 cm) with a mixture of benzene and ether (95 : 5). The corresponding zones were collected, the product eluted and the solvent evaporated. The residue was crystallized from aqueous methanol to afford the alcohol *XXI* (130 mg), m.p. 166–167°C, $[\alpha]_D^{20}$ +2° (*c* 1·7). IR spectrum: 1250, 1657, 1712, 1728, 3030, 3550, 3638 cm^{-1}. ^{1}H-NMR spectrum: 0·71 (3 H, s, 18-H), 1·10 (3 H, s, 19-H), 1·95 (3 H, s, CH_3COO), 4·74 (1 H, t, J = 2·4 Hz, 6α-H). For $C_{29}H_{48}O_3$ (444·7) calculated: 78·33% C, 10·88% H; found: 78·33% C, 10·84% H.

5α-Cholest-2-ene-5,6β-diol 6-Monobenzoate (*XXII*)

The mesylate *XXV* (5 g) in *sym*-collidine (25 ml) was refluxed under nitrogen for 1 h. The mixture was worked up as given for *III*. The residue was crystallized from aqueous ethanol to yield the olefin *XXII* (3·2 g), m.p. 126–127°C, $[\alpha]_D^{20}$ +30° (*c* 2·0), in accordance with the literature[12]. IR spectrum: 1276, 1496, 1586, 1604, 1654, 1722, 3540, 3608 cm^{-1}. ^{1}H-NMR spectrum: 0·70 (3 H, s, 18-H), 1·20 (3 H, s, 19-H), 5·12 (1H, m, $W_{1/2}$ = 5 Hz, 6α-H).

5α-Cholest-2-ene-5,6β-diol 5-Acetate 6-Benzoate (*XXIII*)

The benzoate *XXII* (750 mg) in acetic acid (10 ml) was acetylated with acetic anhydride (1 ml) in the presence of *p*-toluenesulfonic acid (100 mg) at room temperature for 2 hours. The mixture was worked up as given for *IV* to yield the noncrystalline diester *XXIII* (730 mg), $[\alpha]_D^{20}$ +4° (*c* 2·7). ^{1}H-NMR spectrum: 0·71 (3 H, s, 18-H), 1·26 (3 H, s, 19-H), 2·01 (3 H, s, CH_3COO). IR spectrum: 1241, 1275, 1660, 1728, 1739 cm^{-1}. For $C_{36}H_{52}O_4$ (548·8) calculated: 78·79% C, 9·55% H; found: 78·76%C, 9·55% H.

5α-Cholestane-3β,5,6β-triol 3-Methanesulfonate 6-Benzoate (*XXV*)

A solution of the alcohol[8] *XXIV* (10 g) in pyridine (50 ml) was treated at 0°C with methanesulfonyl chloride (5 ml) and allowed to stand at 0°C for 30 min. The mixture was decomposed with ice, diluted with water, the product taken up in ether, and the ethereal solution was worked up as usual. The residue was crystallized from methanol to afford the mesylate *XXV* (7·5 g), m.p. 122–124°C, $[\alpha]_D^{20}$ −35° (chloroform–methanol 1 : 1, *c* 1·8). IR spectrum: 1178, 1274, 1366, 1722, 3510, 3595 cm^{-1}. ^{1}H-NMR spectrum: 0·68 (3 H, s, 18-H), 1·35 (3 H, s, 19-H), 2·94 (3 H, s, CH_3SO_3). For $C_{35}H_{54}O_6S$ (602·9) calculated: 69·73% C, 9·03% H, 5·32% S; found: 69·62% C, 8·95% H, 5·33% S.

6β-Chloro-5α-cholestane-3β,5-diol 3-Methanesulfonate (*XXVII*)

The alcohol[13] *XXVI* (9 g) was dissolved in pyridine (30 ml), treated with methanesulfonyl chloride (5 ml) at 0°C and allowed to stand at room temperature for 45 min. The mixture was worked up as given for *II*. The residue was crystallized from aqueous methanol to yield the mesylate *XXVII* (5·6 g), m.p. 133–134°H (dec.), $[\alpha]_D^{20}$ −21° (*c* 2·1). For $C_{28}H_{49}ClO_3S$ (517·2) calculated: 65·02% C, 9·55% H, 6·85% Cl, 6·20% S; found: 65·11% C, 9·67% H, 6·69% Cl, 6·13% S.

6β-Chloro-5α-cholest-2-en-5-ol (*XXIX*)

Pure 5,6α-epoxy-5α-cholestan-3β-ol 3-toluenesulfonate (100 mg), obtained by crystallization of a mixture of epoxides *X* from acetone–methanol–water, in *sym*-collidine (1·5 ml) was refluxed under nitrogen 1 h. Collidine was distilled off under reduced pressure, the residue was diluted with water and 5% aqueous hydrochloric acid, and the product was extracted with ether. The ethereal solution (c. 50 ml) was shaken with concentrated hydrochloric acid (20 ml) for 10 min, washed with water and 5% aqueous potassium hydrogen carbonate solution, dried and ether was evaporated. The residue was crystallized from aqueous ethanol to yield the chlorohydrin *XXIX* (45 mg), m.p. 73–75°C (literature reports[12] 76–77°C), $[\alpha]_D^{20}$ +4° (*c* 4·7). ^{1}H-NMR spectrum: 0·72 (3 H, s, 18-H), 1·15 (3 H, s, 19-H). IR spectrum: 1 655, 3 035, 3 475, 3 600 cm^{-1}.

The analyses were carried out in the Analytical Laboratory of this Institute (under the direction of Dr J. Horáček). The IR *spectra were recorded by Mrs K. Matoušková and Mr P. Formánek and interpreted by Dr S. Vašíčková, the mass spectra by Dr A. Trka.* ^{1}H-NMR *spectra were recorded by Drs M. Buděšinský, M. Synáčková and M. Masojídková.*

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