# ON STEROIDS. CLIII.* 5,7-CYCLOSTEROIDS. VII.** THE EPIMERIC 1,2-EPOXIDES OF THE 5,7β-CYCLOSTEROID SERIES

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Received August 21st, 1972

The syntheses of the epimeric 1,2-epoxides of the 5,7β-cyclo-5β-cholestane are described and chemical as well as spectral evidence for the structures of the compounds prepared is presented. The conformation of ring A in these compounds is discussed on the basis of the NMR spectra.

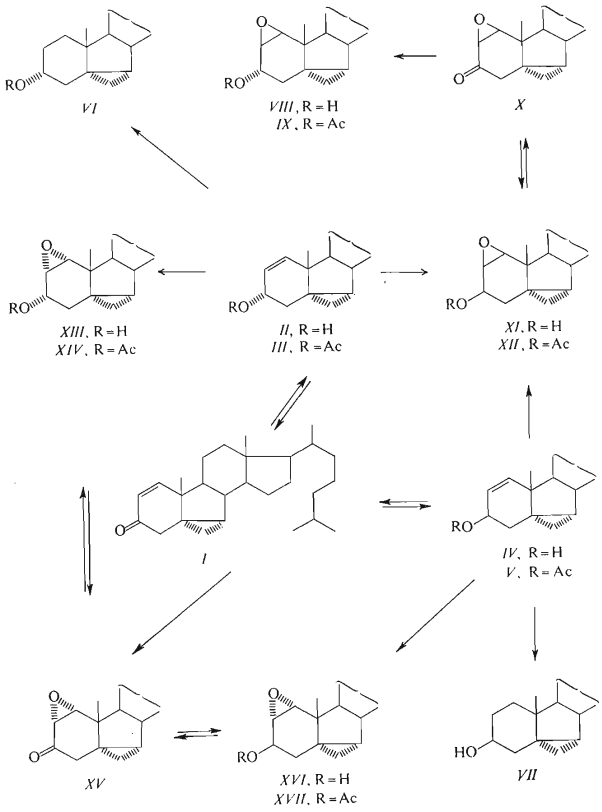
In connection with our studies dealing with 5,7-cyclosteroids substituted in position 1 with an oxygen function the 1,2-epoxides were of interest as convenient starting material. In addition these compounds promised to be interesting also from the stereochemical point of view: Dreiding models suggest that the A-ring exists in a rather distorted and rigid conformation. In this paper we describe the syntheses of the epimeric 1,2-epoxides derived from the 3α- and 3β-hydroxy as well as 3-oxo-5,7β-cyclo-5β-cholestane and discuss their stereochemistry on the basis of the NMR spectra.

The starting compounds were the unsaturated ketone[1] *I* and the allylic alcohols *II* and *IV* obtained from the ketone *I* on metal hydride reduction. The configurations of the hydroxyl groups in these unsaturated alcohols were proved by hydrogenation to the known saturated derivatives *VI* and *VII* (ref.[2]).

When the 3α-hydroxy derivative *II* was epoxidised with peracid the epoxide *XIII* was obtained in excellent yield and only traces of the epimeric epoxide *VIII* were detected. Acetylation gave the corresponding acetate *XIV* which was also obtained on epoxidation of the acetate *III*. Oxidation of the alcohol *XIII* with Jones' reagent yielded the epoxy-ketone *XV*. This compound was also obtained on epoxidation of the unsaturated ketone *I* with alkaline hydrogen peroxide as the sole product. Epoxidation of the 3β-alcohol *IV* with peracid afforded the β-epoxide *XI* accompanied with about 10% of the α-epoxide *XVI*. Separation was possible after oxidation to the epoxy-ketones *X* and *XV*. The pure β-epoxide *XI* was prepared from the ketone *X* on metal hydride reduction after separation from the 3α-epimer *VIII*. Epoxidation of the 3β-acetate *V*, on the other hand, lead exclusively to the α-epoxide *XVII*, which

* Part CLII: This Journal *38*, 1398 (1973).

** Part VI: This Journal *37*, 3483 (1972).




in turn has been obtained on acetylation of the alcohol *XVI* obtained on metal hydride reduction from the ketone *XV*.

The configuration of the epoxide ring in these compounds follows from the NMR evidence (Table I) as well as from the observed stereochemical course of the epoxidation of the allylic alcohols and acetates. The 1,2 double bond is epoxidised as usual predominantly from the less hindered α-face of the molecule with the only exception

of the 3β-alcohol *XI* where the β-epoxide was formed in about 90% yield. This directive influence of the configuration of the allylic hydroxyl on the sterical course of the epoxidation of the double bond has been ascribed to formation of a hydrogen bonding between the peracid and the allylic hydroxyl group and follows well the observations described by Henbest and coworkers[3].

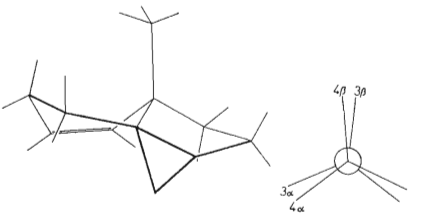



FIG. 1
Twist-Boat Conformation of the A-Ring

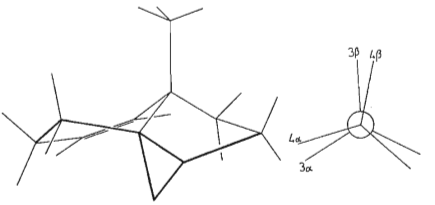



FIG. 2
Twist-Chair Conformation of the A-Ring

As far as the conformation of the A-ring in these compounds is concerned, models suggest a highly rigid boat form (Fig. 1). However, this is not in agreement with the NMR evidence which points rather to a twisted chair as presented by Fig. 2. The NMR results are summarised in Table I. In all of the 3α-oxygenated compounds the coupling constant $J_{3\alpha,4\beta}$ has been found to be zero which is consistent only with the twist chair conformation of ring A in which the angle between the 3β and 4α bonds is about 90°. In agreement with this conformation of ring A are also the close to zero coupling constants $J_{2\alpha,3\beta}$ and $J_{2\alpha,3\beta}$ in the epimeric epoxides.

TABLE I

Characteristic Parameters of NMR Spectra of the Olefins and Epoxides

| Compound | Chemical Shifts[a], p.p.m. | | | | | | Coupling Constants, Hz | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1-H 2-H | 3-H | 4-H | 6-H[b] 18-H | 19-H[c] 21-H | 26-H[b] 27-H | $J_{1,2}$ $J_{2,3}$ | $J_{3,4}$ | $J_{6,6}$[b] $J_{6,7}$ |
| *VI* | [e] | 4·05 m | [e] | 0·02 dd | 0·88 s | 0·85 d | [e] | [e] | 4·3 |
| | [e] | W≈20 Hz | | 0·64 s | 0·90 d | | [e] | | 7·8 |
| *VII* | [e] | 3·79 h | [e] | −0·24 dd | 0·91 s | 0·85 d | [e] | [e] | 4·9 |
| | [e] | W≈31 Hz | | 0·63 s | 0·89 d | | [e] | | 7·5 |
| *VI* | [e] | 5·06 p | [e] | −0·14 dd | 0·89 s | 0·86 d | [e] | [e] | 5·2 |
| acetate | [e] | W≈11 Hz | | 0·64 s | 0·90 d | | [e] | | 7·3 |
| *VII* | [e] | 4·87 h | [e] | −0·15 dd | 0·92 s | 0·85 d | [e] | [e] | 5·1 |
| acetate | [e] | W≈31 Hz | | 0·63 s | 0·89 d | | [e] | | 7·7 |
| *II* | 5·99 d | 4·24 bt | 2·65 dd | 0·06 dd | 0·91 s | 0·85 d | 9·5 | ∓ 0 < 1 | 4·7 |
| | 5·69 dd | | [e] | 0·64 s | 0·89 d | | 3·7 | 5·2 | 7·9 |
| *IV* | 5·89 dd | 4·39 m | 2·25 dd | 0·19 dd | 1·00 s | 0·84 d | 9·5 | 9·1 | 5·0 |
| | 5·48 dd | | ≈1·68 m | 0·63 s | 0·89 d | | 2·1 | 6·8 | 7·6 |
| *III* | 6·15 bd | 5·39 bt | 2·72 dd | −0·03 dd | 0·92 s | 0·85 d | 9·3 | ∓ 0 < 1 | 4·8 |
| | 5·55 dd | | [e] | 0·64 s | 0·89 d | | 3·7 | 5·6 | 7·8 |
| *V* | 5·97 | 5·45 | 2·36 dd | 0·09 dd | 1·02 s | 0·85 d | ≈ 10 | ≈9 | 5·0 |
| | 5·41 | | [e] | 0·64 s | 0·89 d | | ≈2 | ≈7 | 7·6 |
| *XIII* | 3·20 d | 4·15 ddd | 2·25 dd | 0·14 dd | 0·93 s | 0·86 d | 3·9 | ≈0 | 4·7 |
| | 3·40 t | | [e] | 0·65 s | 0·90 d | | 4·1 | 5·7 | 7·3 |
| *XVI* | 3·04 t | 4·15 t | ≈1·95 m | −0·12 dd | 1·03 s | 0·85 d | 3·7 | 8·8 | 5·4 |
| | | | ≈1·38 m | 0·64 s | 0·89 d | | ∓0 ≪ 0·4 | 7·6 | 7·7 |
| *XIV* | 3·09 d | 5·29 dd | 2·44 dd | 0·12 dd | 0·94 s | 0·85 d | 3·8 | ≈0 | ≈5 |
| | 3·37 t | | [e] | 0·64 s | 0·90 d | | 4·0 | 6·8 | ≈7·5 |
| *XVII* | 3·02 s | 5·10 t | ≈2·05 m | −0·04 dd | 1·04 s | 0·85 d | [e] | 9·4 | 5·3 |
| | | | ≈1·47 m | 0·64 s | 0·90 d | | ≈0 | 8·0 | 7·3 |
| *VIII* | 3·02 d | 4·27 bd | 2·30 dd | 0·00 dd | 0·89 s | 0·85 d | 3·4 | ≈0 | 4·9 |
| | 3·11 bd | | [e] | 0·65 s | 0·90 d | | ∓0 ≪ 0·3 | 4·6 | 7·8 |
| *XI* | 3·13 d | 4·06 ddd | ≈1·81 m | −0·31 dd | 0·99 s | 0·85 d | 3·7 | 9·2 | 4·9 |
| | 3·28 t | | ≈1·37 m | 0·64 s | 0·89 d | | 2·6 | 6·8 | 7·7 |
| *IX* | 3·04 s | 5·30 d | 2·29 dd | −0·07 dd | 0·88 s | 0·85 d | [e] | ≈0 | 5·5 |
| | | | [e] | 0·64 s | 0·89 d | | ≈0 | 4·7 | 7·5 |
| *XIX* | 3·07 d | 5·22 ddd | [e] | −0·22 dd | 1·01 s | 0·85 d | 3·8 | 9·5 | ≈5 |
| | 3·29 t | | [e] | 0·64 s | 0·89 d | | 2·6 | 6·9 | ≈7·5 |

[a] All NMR spectra were measured in chloroform ($CHCl_3$ as internal reference). The values of chemical shifts are given in $\delta$-scale (p.p.m.) and corrected on tetramethylsilane ($\delta_{CHCl_3} = 7{\cdot}25$ p.p.m.). For characterisation of the signals following abbreviations are used: b broad, s singlet, d doublet, dd doublet of doublets, t triplet, m multiplet, W with of the multiplet, h heptet, p pentet. [b] Only one of the cyclopropane protons is observable out of the steroid envelope. Coupling constants $J_{6,6}$ and $J_{6,7}$ were obtained from the signal splitting of this proton. [c] $J_{20,21} = 5{\cdot}6$ Hz for compounds *I*—*XIX*. [d] $J_{25,26} = J_{25,27} = 6{\cdot}0$ Hz for compounds *I*—*XIX*. [e] Indeterminable value. [f] $J_{3,OH} = 11{\cdot}3$ Hz.

## 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°C. The infrared 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. 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% HCl water, 5% $NaHCO_3$ and water, drying with magnesium sulphate, and evaporation of the solvent.

3-Oxo-5,7β-cyclo-5β-cholest-1-ene (*I*)

a) *From* 3α-*hydroxy*-5,7β-*cyclo*-5β-*cholest*-1-*ene* (II): The alcohol *II* (75 mg) in acetone (2·5 ml) was treated with excess Jones' reagent and allowed to stand for 15 min. Methanol was added to remove the excess oxidising agent, the reaction mixture was diluted with water, and the product taken into ether. The ethereal solution was washed with water, a sodium hydrogen carbonate solution, water, dried, and evaporated. The residue was crystallised from ethanol–methanol to yield 55 mg of the ketone *I*, m.p. 80—81°C, $[\alpha]_D^{20}$ +73° (*c* 1·03), identical with the authentic[1] sample.

b) *From* 3β-*hydroxy*-5,7β-*cyclo*-5β-*cholest*-1-*ene* (IV): The alcohol *IV* (80 mg) was oxidised with Jones' reagent in acetone as given in the previous experiment. Similar working up and crystallisation from the same solvent mixture yielded 60 mg of the ketone *I*, m.p. 79—81°C, $[\alpha]_D^{20}$ +77° (*c* 1·15), identical with the authentic[1] sample.

3α-Hydroxy-5,7β-cyclo-5β-cholest-1-ene (*II*)

The ketone[1] *I* (600 mg) in ether (40 ml) was treated at 0°C with a solution of lithium aluminium hydride (150 mg) in the same solvent and allowed to stand for 10 min. The excess hydride was decomposed with ethyl acetate a saturated solution of sodium sulphate was added, and the product was isolated with ether. Working up gave 580 mg of a product which contained according to the thin-layer chromatography two components. It was chromatographed on a silica gel column (80 g) in benzene and fractions containing the lipophilic component were combined and evaporated. The residue was crystallised from methanol–water to yield 120 mg of the alcohol *II*, m.p. 79—80°C, $[\alpha]_D^{20}$ −66° (*c* 1·82). For $C_{27}H_{44}O$ (384·6) calculated: 84·31% C, 11·53% H; found: 84·16% C, 11·32% H.

3α-Acetoxy-5,7β-cyclo-5β-cholest-1-ene (*III*)

The alcohol *II* (180 mg) was acetylated with acetic anhydride (0·8 ml) in pyridine (1 ml) at room temperature for 18 h. The reaction mixture was decomposed with ice, and the product isolated with ether. Working up and crystallisation from methanol gave 132 mg of the acetate *III*, m.p. 72—73°C, $[\alpha]_D^{20}$ −63° (*c* 1·12). For $C_{29}H_{46}O_2$ (426·7) calculated: 81·63% C, 10·87% H; found: 81·49% C, 10·82% H.

3β-Hydroxy-5,7β-cyclo-5β-cholest-1-ene (*IV*)

Elution of the chromatography after isolation of the 3α-epimer *II* with the same solvent afforded fractions containing the polar 3β-alcohol. Combination, evaporation, and crystallisation from methanol–water gave 395 mg of the alcohol *IV*, m.p. 113°C, $[\alpha]_D^{20}$ +6° (*c* 1·28). For $C_{27}H_{44}O$ (384·6) calculated: 84·31% C, 11·53% H; found: 84·28% C, 11·41% H.

3β-Acetoxy-5,7β-cyclo-5β-cholest-1-ene (*V*)

The alcohol *IV* (120 mg) was acetylated with acetic anhydride (1·5 ml) in pyridine (2 ml) for 18 h at room temperature. The reaction mixture was poured on ice, the product isolated with ether, and worked up. The residue was crystallised from methanol to yield 103 mg of the acetate *V*, m.p. 89–90°C, $[\alpha]_D^{20}$ +28° (*c* 1·79). For $C_{29}H_{46}O_2$ (426·7) calculated: 81·63% C, 10·87% H; found: 81·57% C, 10·83% H.

5,7β-Cyclo-5β-cholestan-3α-ol (*VI*)

The unsaturated alcohol *II* (65 mg) in glacial acetic acid (4 ml) was hydrogenated over Adams' catalyst for 2 h. The catalyst was filtered off, washed with ether, and the filtrate was evaporated under reduced pressure. The residue was dissolved in ether, the ethereal solution was washed with a sodium hydrogen carbonate solution, water, dried, and evaporated. The residue was crystallised from methanol to yield 38 mg of the alcohol *VI*, m.p. 110–111°C, $[\alpha]_D^{20}$ −41° (*c* 1·18), identical with the authentic[2] sample.

5,7β-Cyclo-5β-cholestan-3β-ol (*VII*)

The alcohol *IV* (50 mg) was hydrogenated in acetic acid over Adams' catalyst as given in the previous experiment. Similar working up and crystallisation from methanol afforded 32 mg of the alcohol *VII*, m.p. 148°C, $[\alpha]_D^{20}$ −23° (*c* 1·23), identical with the authentic[2] sample.

1β,2β-Epoxy-5,7β-cyclo-5β-cholestan-3α-ol (*VIII*)

The ketone *X* (1 g) in tetrahydrofuran (25 ml) was treated at 0°C with solid lithium tri-tert-butoxyaluminium hydride (2 g) and allowed to stand at room temperature for 1 h. The reaction mixture was diluted with ether, the solution was washed with acetic acid (2%), a sodium hydrogen carbonate solution, water, dried, and evaporated. The residue consisted according to the thin-layer chromatography of two components in about equal quantities. The mixture was chromatographed preparatively on 6 plates of silica gel (40 × 20 cm) in benzene–ether (4 : 1). The zones containing the lipophilic compounds were collected, the product was extracted with ether, and the extract evaporated. The residue on crystallisation from methanol–water yielded 380 mg of the alcohol *VIII*, m.p. 128°C, $[\alpha]_D^{20}$ −28° (*c* 1·86). For $C_{27}H_{44}O_2$ (400·6) calculated: 80·94% C, 11·07% H; found: 80·80% C, 10·95% H.

1β,2β-Epoxy-3α-acetoxy-5,7β-cyclo-5β-cholestane (*IX*)

The alcohol *VIII* (170 mg) was acetylated with acetic anhydride (1·5 ml) in pyridine (2 ml) for 18 h at room temperature. The reaction mixture was poured on ice, the product extracted into ether, and the ethereal solution was worked up. The residue after evaporation of the solvent was crystallised from methanol to yield 125 mg of the acetate *IX*, m.p. 111–112°C, $[\alpha]_D^{20}$ +9° (*c* 1·82). For $C_{29}H_{46}O_3$ (442·7) calculated: 78·68% C, 10·48% H; found: 78·56% C, 10·46% H.

1β,2β-Epoxy-5,7β-cyclo-5β-cholestan-3-one (*X*)

The alcohol *IV* (400 mg) in ether (40 ml) was treated with perphthalic acid (300 mg) in the same solvent (5 ml) and allowed to stand at room temperature for 30 h. The reaction mixture was diluted with ether, the excess peracid was extracted into 5% $Na_2CO_3$, the ethereal solution was washed with water, dried, and evaporated. The residue showed one spot on TLC with traces of polar

as well as lipophilic impurities. It was chromatographed on a silica gel column (50 g) in benzene yielding after working up of the corresponding fractions and evaporation of the solvent 380 mg of a chromatographically pure solid m.p. 167—168°C. The product was dissolved in acetone (8 ml) and treated with excess Jones' reagent. After 15 minutes at room temperature methanol was added to destroy the excess chromic acid, the reaction mixture was diluted with ether, washed with water, a sodium hydrogen carbonate solution, water, dried, and evaporated. TLC showed presence of about 10% of the α-epoxide *XV* (polar component) in the product. It was chromatographed preparatively on four plates of silica gel (40 cm × 20 cm) in benzene–ligroin (3 : 1). The zones with the lipophilic component were collected, the product extracted with ether, and the solvent was evaporated to leave 312 mg of the purified product. Crystallisation from diluted ethanol gave 268 mg of the ketone *X*, m.p. 93—94°C, $[\alpha]_D^{20}$ +37° (*c* 1·13). For $C_{27}H_{42}O_2$ (398·6) calculated: 81·35% C, 10·62% H; found: 81·22% C, 10·64% H.

1β,2β-Epoxy-5,7β-cyclo-5β-cholestan-3β-ol (*XI*)

The zones containing the polar component (after isolation of the 3α-epimer *VIII*) were collected, the product extracted with ether, and the solvent was evaporated. The residue was crystallised from methanol to yield 440 mg of the alcohol *XI*, m.p. 170—171°C, $[\alpha]_D^{20}$ +2° (*c* 1·95). For $C_{27}H_{44}O_2$ (400·6) calculated: 80·94% C, 10·07% H; found: 80·76% C, 10·94% H.

3β-Acetoxy-1β,2β-epoxy-5,7β-cyclo-5β-cholestane (*XII*)

The alcohol *XI* (200 mg) was acetylated with acetic anhydride (1·5 ml) in pyridine (2 ml) at room temperature for 18 h. The reaction mixture was decomposed with ice, the product was isolated with ether, and the residue after evaporation of the solvent was crystallised from methanol. Yield 170 mg of the acetate *XII*, m.p. 119—120°C, $[\alpha]_D^{20}$ +24° (*c* 1·92). For $C_{29}H_{46}O_3$ (442·7) calculated: 78·68% C, 10·48% H; found: 78·63% C, 10·39% H.

1α,2α-Epoxy-5,7β-cyclo-5β-cholestan-3α-ol (*XIII*)

a) *From* 1α,2α-*epoxy*-5,7β-*cyclo*-5β-*cholestan*-3-*one* (XV): A solution of the ketone *XV* (300 mg) in tetrahydrofuran (10 ml) was treated at 0°C with lithium tri-tert-butoxyaluminium hydride (600 mg) and allowed to stand at room temperature for 2 h. The reaction mixture was diluted with ether, the excess hydride was decomposed with acetic acid, and the ethereal solution was worked up. The residue after evaporation of the solvent contained according to the thin-layer chromatography two components. It was chromatographed on a silica gel column (30 g) in benzene. Fractions containing the lipophilic component were combined, evaporated, and the residue was crystallised from methanol–water to yield 85 mg of the alcohol *XIII*, m. p. 99—100°C, $[\alpha]_D^{20}$ −49° (*c* 0·89). For $C_{27}H_{44}O_2$ (400·6) calculated: 80·94% C, 11·07% H; found: 80·79% C, 10·93% H.

b) *From* 3α-*hydroxy*-5,7β-*cyclo*-5β-*cholest*-1-*ene* (II): A solution of the alcohol *II* (300 mg) in chloroform (6 ml) was treated with *m*-chloroperbenzoic acid (300 mg) and allowed to stand at room temperature for 30 min. The reaction mixture was diluted with ether, the excess peracid was extracted into 5% $Na_2CO_3$ and the ethereal solution was washed with water, dried, and evaporated. The residue contained according to the thin-layer chromatography next to the desired α-epoxide traces of the β-epoxide *VIII*. Purification was carried out on two plates of silica gel (40 cm × 20 cm) in benzene–ether (4 : 1). The zones with the main product were collected, the product was eluted with ether, and the solvent was evaporated. The residue was crystallised from methanol–water to yield 265 mg of the epoxide *XIII*, m.p. 99—100°C, $[\alpha]_D^{20}$ −52° (*c* 1·19).

3α-Acetoxy-1α,2α-epoxy-5,7β-cyclo-5β-cholestane (*XIV*)

a) *From* 3α-*acetoxy*-5,7β-*cyclo*-5β-*cholest*-1-*ene* (III): The acetate *III* (120 mg) in chloroform (3 ml) was treated with *m*-chloroperbenzoic acid (100 mg) as described in the previous experiment. Similar working up and crystallisation of the crude product from methanol gave 80 mg of the epoxide *XIV*, m.p. 99—100°C, $[\alpha]_D^{20}$ −51° (*c* 1·43). For $C_{29}H_{46}O_3$ (442·7) calculated: 78·68% C, 10·48% H; found: 78·61% C, 10·37% H.

b) *From* 1α,2α-*epoxy*-5,7β-*cyclo*-5β-*cholestan*-3α-*ol* (XIII): The alcohol *XIII* (80 mg) was acetylated with acetic anhydride (0·5 ml) in pyridine (0·7 ml) for 18 h at room temperature. Usual working up and crystallisation from methanol gave 63 mg of the acetate *XIV*, m.p. 99 to 100°C, $[\alpha]_D^{20}$ −53° (*c* 1·24).

1α,2α-Epoxy-5,7β-cyclo-5β-cholestan-3-one (*XV*)

a) *From* 3-*oxo*-5,7β-*cyclo*-5β-*cholest*-1-*ene* (I): A solution of the ketone *I* (700 mg) in dioxan (30 ml) was treated with 30% hydrogen peroxide (2·5 ml) and 5% NaOH (7 ml) under stirring. After 20 h the reaction mixture was diluted with water, the crystalline product was taken into dichloromethane–ether, the organic layer was washed with water, dried, and evaporated. The residue was chromatographed on a silica gel column (200 g) in benzene. The corresponding fractions were combined, evaporated, and the residue was crystallised from methanol–ethanol to yield 360 mg of the epoxide *XV*, m.p. 139—140°C, $[\alpha]_D^{20}$ +98° (*c* 1·02). For $C_{27}H_{42}O_2$ (398·6) calculated: 81·35% C, 10·62% H; found: 81·39% C, 10·79% H.

b) *From* 1α,2α-*epoxy*-5,7β-*cyclo*-5β-*cholestan*-3β-*ol* (XVI): The alcohol *XVI* (75 mg) in acetone (2 ml) was treated with excess Jones' reagent and allowed to stand at room temperature for 15 min. The excess oxidising agent was removed with methanol, the reaction mixture was diluted with ether, the ethereal solution was washed with water, a sodium hydrogen carbonate solution, water, dried, and evaporated. The residue was crystallised from ethanol–methanol to yield 52 mg of the ketone *XV*, m.p. 141—142°C, $[\alpha]_D^{20}$ +102° (*c* 1·43).

c) *From* 1α,2α-*epoxy*-5,7β-*cyclo*-5β-*cholestan*-3α-*ol* (XIII): The alcohol *XIII* (85 mg) in acetone (2 ml) was oxidised with Jones' reagent as described in the previous experiment. Similar working up and crystallisation from the same solvent mixture afforded 60 mg of the ketone *XV*, m.p. 140—141°C, $[\alpha]_D^{20}$ +97° (*c* 1·18).

d) *From* 3β-*hydroxy*-5,7β-*cyclo*-5β-*cholest*-1-*ene* (IV): The zones containing the polar component after isolation of the β-epoxide *X* were collected, the product eluted with ether, and the solvent was evaporated. The residue was crystallised from methanol–ethanol to yield 26 mg of the ketone *XV*, m.p. 140—141°C, $[\alpha]_D^{20}$ +101° (*c* 1·02).

1α,2α-Epoxy-5,7β-cyclo-5β-cholestan-3β-ol (*XVI*)

Elution of the chromatography after isolation of the 3α-epimer *XIII* with the same solvent afforded fractions with the polar component. Combination, evaporation, and crystallisation of the residue from methanol–water yielded 142 mg of the alcohol *XVI*, m.p. 135—136°C, $[\alpha]_D^{20}$ −14° (*c* 1·15). For $C_{27}H_{44}O_2$ (400·6) calculated: 80·94% C, 11·07% H; found: 80·86% C, 10·88% H.

3β-Acetoxy-1α,2α-epoxy-5,7β-cyclo-5β-cholestane (*XVII*)

a) *From* 3β-*acetoxy*-5,7β-*cyclo*-5β-*cholest*-1-*ene* (V): The acetate *V* (150 mg) in chloroform (5 ml) was treated with *m*-chloroperbenzoic acid (120 mg) and allowed to stand at room temper-

ature for 3 days. The reaction mixture was diluted with ether, the excess peracid was extracted into 5% $Na_2CO_3$, and the ethereal solution was washed with water, dried, and evaporated. The residue was purified on one silica gel plate (40 cm × 20 cm) in benzene. Working up of the corresponding zones and crystallisation from methanol yielded 105 mg of the epoxide *XVII*, m.p. 121–122°C, $[\alpha]_D^{20}$ −18° (*c* 1·32). For $C_{29}H_{46}O_3$ (442·7) calculated: 78·68% C, 10·48% H; found: 78·81% C, 10·43% H.

b) *From* 1α,2α-*epoxy*-5,7β-*cyclo*-5β-*cholestan*-3β-*ol* (XVI): The alcohol *XVI* (110 mg) was acetylated with acetic anhydride (0·5 ml) in pyridine (0·7 ml) for 18 h at room temperature. Usual working up and crystallisation from methanol gave 87 mg of the acetate *XVII*, m.p. 123–124°C, $[\alpha]_D^{20}$ −16° (*c* 1·15).

*The analyses were carried out in the Analytical Laboratory of this Institute by Mr V. Štěrba, Mrs E. Šipová, and Mrs E. Sýkorová under the direction of Dr J. Horáček. The IR spectra were recorded by Mrs S. Vašíčková under the direction of Dr J. Smolíková.*

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Translated by the author (J.F.).