ON STEROIDS. CXLIV.*

6-HYDROXYLATED B-NORCHOLESTANE DERIVATIVES

J.Joska, J.Fajkoš and F.Šorm

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

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Fission of the 5α,6α-epoxide in the B-norcholestane series with perchloric acid has been studied and the structure of the products established by chemical means.

In the course of our studies of the relationship between structure and biological activity of steroids we became interested in the 6-oxygenated B-norsteroids.

Some of these compounds have been prepared previously[1-4] in our Laboratory by various routes but a more efficient method was required for the syntheses of the key-model compounds *XIII* and *XXVI*. The most convenient starting compound is the 5α,6α-epoxide[5] *I* which may easily be prepared in large quantities. Unfortunately, the cleavage of this epoxide represents a difficult step and usually[1,6] Wagner-Meerwein rearrangement takes place giving rise to the 5-methyl derivative *II* as to the main product. Different results have now been obtained when the epoxide was cleaved with perchloric acid and the desired product *IV* with the normal B-norsteroid skeleton was isolated in pure state in about 70% yield next to the rearrangement derivative *II* (10%). The structure of the acetate *IV* was proved by its conversion to the mesylate *VI* followed by hydride reduction to the known[7] diol *VIII*. The structure follows also from the subsequent reaction: The monoacetate *IV* was hydrolysed to the triol *III* which on oxidation with Jones'reagent gave the dione *IX*. Reflux with acetic acid yielded the known[1] unsaturated dione *X*.

The 6α-hydroxy derivative *XIII* was prepared as follows: The monoacetate *IV* was transformed to the diacetate *V* which was partially hydrolysed to the monoacetate *VII*. Its oxidation led to the ketone *XI* which on alkali treatment afforded the dione[8] *XII*; milder conditions, however, led directly to the desired 6α-hydroxy unsaturated ketone[2] *XIII*. This alcohol was also obtained by hydrolysis of the acetate[2] *XIV* prepared from the alcohol *XI* by reflux with acetic acid.

The acetate *IV* served also as the starting material for the synthesis of the epimeric 6β-alcohol *XXVI*: It was oxidised to the ketone[3] *XVI* which on catalytic hydrogena-

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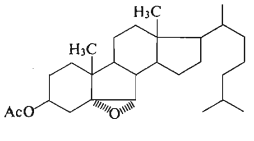
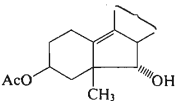
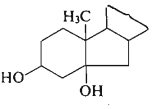
tion afforded the 6β-hydroxy derivative *XVIII*, characterised also as the triol *XVII* and the diacetate *XIX*. The triol *XVII* on oxidation gave again the dione *IX*. In the next step the 6β-hydroxyl in the alcohol *XVIII* was protected by benzoylation, the acetoxy group at $C_{(3)}$ was hydrolysed partially to the alcohol *XXII* and the free



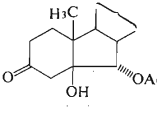
I



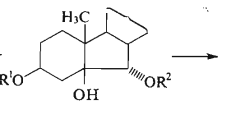
II



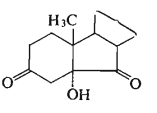
VIII



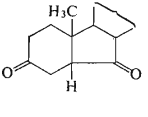
XI



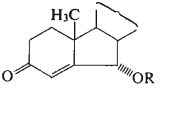
III, $R^1 = R^2 = H$
IV, $R^1 = Ac$; $R^2 = H$
V, $R^1 = R^2 = Ac$
VI, $R^1 = Ac$; $R^2 = CH_3SO_2$
VII, $R^1 = H$; $R^2 = Ac$



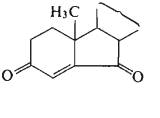
IX



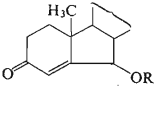
XII



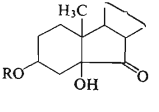
XIII, R = H
XIV, R = Ac



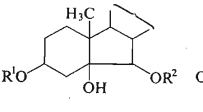
X



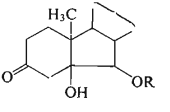
XXVI, R = H
XXVII, R = Ac



XV, R = H
XVI, R = Ac



XVII, $R^1 = R^2 = H$
XVIII, $R^1 = Ac$; $R^2 = H$
XIX, $R^1 = R^2 = Ac$
XX, $R^1 = Ac$; $R^2 = CH_3SO_2$
XXI, $R^1 = Ac$; $R^2 = C_6H_5CO$
XXII, $R^1 = H$; $R^2 = C_6H_5CO$



XXIII, R = H
XXIV, R = Ac
XXV, $R = C_6H_5CO$

hydroxyl oxidised to the ketone *XXV*. Hydrolysis to the diol *XXIII* followed by reflux with acetic acid gave the desired alcohol[4] *XXVI*. Similarly, the monoacetate *XXIV* afforded the acetate *XXVI* when treated with acetic acid. We expect to utilise the results obtained in this work for the syntheses of 6-oxygenated B-noranalogues of androgens.

EXPERIMENTAL

Melting points were determined on a Kofler block. Analytical samples were dried at 80°C/0,2 Torr. Optical rotation was measured in chloroform unless otherwise stated. The IR measurements were carried out in tetrachloromethane. The identity of samples prepared by different routes was checked by mixture-melting points, by thin layer chromatography and by IR spectra.

3β-Acetoxy-5β-methyl-19,B-bisnorcholest-9-en-6α-ol (*II*)

The epoxide[5] *I* (3 g) in acetone (120 ml) and water (6 ml) was treated with 70% $HClO_4$ (2·5 ml) and allowed to stand at room temperature for 2 h. The excess acid was neutralised with a $NaHCO_3$ solution, acetone distilled off under reduced pressure and the product taken into ether. The ethereal solution was washed with water, dried, and evaporated. The residue was chromatographed on a silica gel column in benzene–ether (19 : 1). Fractions containing the lipophilic component were combined, evaporated, and the residue crystallised from ligroin (b.p. 40—60°C) to yield 310 mg of the acetate *II*, m.p. 100—101°C, $[\alpha]_D^{20}$ +67° (*c* 1·17), identical with the compound described previously[1].

5β-B-Norcholestane-3β,5,6α-triol (*III*)

The acetate *IV* (100 mg) in methanol (5 ml) was treated with K_2CO_3 (80 mg) in water (1 ml) and refluxed for 2 h. Methanol was distilled off under reduced pressure, the residue diluted with water, and the product isolated with ether. Working up and crystallisation from ethyl acetate afforded 62 mg of the triol *III*, m.p. 154—156°C, $[\alpha]_D^{20}$ +14° (*c* 1·15 in ethanol). For $C_{26}H_{46}O_3$ (406·6) calculated: 76·79% C, 11·40% H; found: 77·08% C, 11·28% H.

3β-Acetoxy-5β-norcholestane-5,6α-diol (*IV*)

Continued elution of the chromatography after isolation of the monoacetate *II* with the same solvent mixture gave fractions containing the polar component. Working up and crystallisation from ligroin (b.p. 40—60°C) yielded 2·01 g of the acetate *IV*, m.p. 108—110°C, $[\alpha]_D^{20}$ +14·2° (*c* 1·41). For $C_{28}H_{48}O_4$ (448·7) calculated: 74·95% C, 10·78% H; found: 75·69% C, 10·71% H.

3β,6α-Diacetoxy-5β-B-norcholestan-5-ol (*V*)

The monoacetate *IV* (400 mg) was acetylated with acetic anhydride (3 ml) in pyridine (4 ml) at 30°C for 3 days. The acetylation mixture was decomposed with ice, the product extracted into ether, and the ethereal solution was washed with dilute hydrochloric acid, a $NaHCO_3$ solution, water, dried and evaporated. The residue was chromatographed over silica gel (60 g) in ligroin (b.p. 40—60°C)–ether (4 : 1). The corresponding fractions were worked up, evaporated, and the residue was crystallised from methanol to give 310 mg of the diacetate *V*, m.p. 122—123°C, $[\alpha]_D^{20}$ +13·4° (*c* 1·76). For $C_{30}H_{50}O_5$ (490·7) calculated: 73·43% C, 10·27% H; found: 73·46% C, 10·07% H.

3β-Acetoxy-6α-methanesulphonyloxy-5β-B-norcholestan-5-ol (*VI*)

The monoacetate *IV* (500 mg) in pyridine (6 ml) was treated with methanesulphonyl chloride (0·8 ml) and allowed to stand at room temperature for 20 h. The reaction mixture was decomposed with ice, the product extracted into ether, the ethereal solution was worked up, and evaporated. The residue was crystallised from ligroin (b.p. 40—60°C) to yield 350 mg of the mesylate *VI*, m.p. 129—130°C, $[\alpha]_D^{20}$ +25° (*c* 1·43). For $C_{29}H_{50}O_6S$ (526·8) calculated: 66·12% C, 9·56% H, 6·08% S; found: 66·24% C, 9·86% H, 5·79% S.

6α-Acetoxy-5β-B-norcholestane-3β,5-diol (*VII*)

The diacetate *V* (340 mg) in methanol (18 ml) was treated with K_2CO_3 (240 mg) in water (3·5 ml) and kept for 15 min at 50°C. The reaction mixture was then diluted with water, the precipitate taken into ether, the ethereal solution was washed with water, dried, and evaporated. The residue was chromatographed on a silica gel column (30 g) in benzene–ether (2 : 1). Working up of the corresponding fractions and crystallisation from methanol gave 270 mg of the diol *VII*, m.p. 121—123°C, $[\alpha]_D^{20}$ −16·5° (*c* 1·44). For $C_{28}H_{48}O_4$ (448·7) calculated: 74·95% C, 10·78% H; found: 75·10% C, 10·95% H.

5β-B-Norcholestane-3β,5-diol (*VIII*)

A solution of the mesylate *VI* (100 mg) in tetrahydrofuran was treated with a solution of lithium-aluminium hydride (200 mg) in the same solvent (8 ml) and refluxed for 8 h. The excess hydride was removed with ethyl acetate, the reaction mixture was diluted with ether, washed with dilute hydrochloric acid, $NaHCO_3$, water, dried, and evaporated. The product was chromatographed on a silica gel column in ligroin (b.p. 40—60°C)–acetone (9 : 1) to yield after working up and crystallisation from methanol 35 mg of the diol *VIII*, m.p. 113—114°C, $[\alpha]_D^{20}$ +21° (*c* 1·08), identical with the compound described previously[7].

5-Hydroxy-5β-B-norcholestane-3,6-dione (*IX*)

a) A solution of the triol *III* (900 mg) in acetone (45 ml) was treated with excess Jones' reagent and stirred for 10 min at room temperature. The excess agent was removed with methanol, the reaction mixture was diluted with ether and water, the ethereal layer was separated and worked up. The resiue after evaporation of the solvent was chromatographed on a silica gel column (100 g) in benzene–ether (4 : 1). The corresponding fractions were worked up, evaporated, and the residue was crystallised from ethyl acetate to yield 315 mg of the dione *IX*, m.p. 175—176°C, $[\alpha]_D^{20}$ −65° (*c* 1·30). For $C_{26}H_{42}O_3$ (402·6) calculated: 77·56% C, 10·52% H; found: 77·55% C, 10·25% H. *b*) The triol *XVII* (150 mg) in acetone (10 ml) was oxidised with Jones' reagent (0·4 ml) as given for the 6α-epimer in the foregoing experiment. Similar working up, chromatography over silica gel, and crystallisation from ethyl acetate gave 92 mg of the dione *IX*, m.p. 175—176°C, $[\alpha]_D^{20}$ −63° (*c* 1·23).

B-Norcholest-4-ene-3,6-dione (*X*)

The alcohol *IX* (100 mg) in acetic acid (8 ml) was refluxed for 3 h, the reaction mixture treated with water, and the product taken into ether. The ethereal solution was washed with a $NaHCO_3$ solution, water, dried, and evaporated. The residue on crystallisation from methanol afforded 39 mg of the dione *X*, m.p. 115—116°C, $[\alpha]_D^{20}$ +171° (*c* 1·87), identical with the compound described previously[1].

6α-Acetoxy-5-hydroxy-5β-B-norcholestan-3-one (*XI*)

A solution of the diol *VII* (255 mg) in acetone (7 ml) was treated with excess Jones' reagent and stirred at room temperature for 15 min. Methanol was added and the product was isolated with ether. Usual working up and crystallisation from ligroin (b.p. 40—60°C) gave 163 mg of the ketone *XI*, m.p. 128—130°C, $[\alpha]_D^{20}$ +35° (*c* 1·42); IR: 3580, 1745, 1711 cm^{-1}. For $C_{28}H_{46}O_4$ (446·7) calculated: 75·29% C, 10·38% H; found: 75·09% C, 10·22% H.

5β-B-Norcholestane-3,6-dione (*XII*)

The acetate *XI* (160 mg) in methanol (5 ml) was treated with KOH (500 mg) in water (10 ml) and refluxed under nitrogen for 5 h. The reaction mixture was diluted with water, the product isolated with ether, and the residue after working up was chromatographed over silica gel (10 g) in benzene–ether (9 : 1). The corresponding fractions were combined, evaporated, and the residue was crystallised from methanol to yield 90 mg of the dione *XII*, m.p. 115—116°C, $[\alpha]_D^{20}$ −36° (*c* 1·27), identical with the authentic[8] sample.

6α-Hydroxy-B-norcholest-4-en-3-one (*XIII*)

A solution of the acetate *XI* (50 mg) in methanol (2 ml) was treated with KOH (150 mg) in the same solvent (3 ml) and the mixture was heated to 50°C for 20 min under nitrogen. The excess alkali was neutralised with acetic acid, the reaction was diluted with water, and the product isolated with ether. Working up, and crystalisation from methanol gave 30 mg of the ketone *XIII*, m.p. 166—168°C, $[\alpha]_D^{20}$ 0° (*c* 1·12), identical with the compound described previously[2].

6α-Acetoxy-B-norcholest-4-en-3-one (*XIV*)

a) The acetate *XI* (50 mg) in acetic acid (4 ml) was refluxed for 3 h. Water was added, the product isolated and the residue after evaporation of the solvent was crystallised from methanol to yield 19 mg of the ketone[2] *XIV*, m.p. 112—113°C, $[\alpha]_D^{20}$ −94° (*c* 1·19). *b*) The alcohol *XIII* (30 mg) was acetylated with acetic anhydride (0·3 ml) in pyridine (0·4 ml) at room temperature for 20 h. The reaction mixture was decomposed with ice and the product isolated with ether. Working up and crystallisation from methanol gave 15 mg of the acetate *XIV*, m.p. 112—113°C, $[\alpha]_D^{20}$ −95° (*c* 1·77), identical with the compound described previously[2].

3β,5-Dihydroxy-5β-B-norcholestan-6-one (*XV*)

The acetate *XVI* (650 mg), in methanol (32 ml) was refluxed with K_2CO_3 (650 mg) in water (3·2 ml) for 2 h. Methanol was distilled off under reduced pressure, the residue treated with water, and the product isolated with ether. The ethereal solution was worked up, and the residue chromatographed over silica gel (60 g) in ligroin (b.p. 40—60°C)–acetone (30 : 1). The corresponding fractions gave after working up and crystallisation from methanol–water 405 mg of the diol *XV*, m.p. 156—158°C, $[\alpha]_D^{20}$ +55° (*c* 1·51), identical with the authentic sample[3].

3β-Acetoxy-5-hydroxy-5β-B-norcholestan-6-one (*XVI*)

a) The diol *IV* (2 g) was oxidised with excess Jones' reagent (4·5 ml) in acetone (80 ml) for 6 min at room temperature. Methanol was added to destroy the excess oxidising agent, the reaction mixture was treated with water, and the product which precipitated was isolated with ether. The ethereal solution was worked up, evaporated, and the residue (2 g) was chromatographed over

silica gel (200 g) in benzene–ether (19 : 1). The corresponding fractions were combined, evaporated, and the product crystallised from methanol–water to yield 1·2 g of the ketone *XVI*, m.p. 92—93°C (some samples melted at 102—104°C), $[\alpha]_D^{20}$ +55° (*c* 1·38), identical with the authentic sample[3]. *b*) The diol *XV* (100 mg) was acetylated with acetic anhydride (0·3 ml) in pyridine (0·4 ml) for 20 h at room temperature. Usual working up and crystallisation from methanol–water gave 50 mg of the acetate *XVI*, m.p. 90—92°C, $[\alpha]_D^{20}$ +56° (*c* 1·43).

5β-B-norcholestane-3β,5,6β-triol (*XVII*)

a) The mesylate *XX* (110 mg) in absolute tetrahydrofuran (4 ml) was treated with a solution of lithiumaluminium hydride (220 mg) in the same solvent and refluxed for 6 h. The excess hydride was decomposed with ethyl acetate and wet ether, the ethereal solution was washed with dilute hydrochloric acid, a sodium hydrogen carbonate solution, water, dried, and evaporated. The residue on chromatography over silica gel (10 g), elution with benzene–ether (9 : 1) and crystallisation from ligroin (b.p. 40—60°C) afforded 32 mg of the triol *XVII*, m.p. 155—156°C, $[\alpha]_D^{20}$ +56° (*c* 1·01). For $C_{26}H_{46}O_3$ (406·6) calculated: 76·79% C, 11·40% H; found: 76·89% C, 11·51% H. *b*) The acetate *XVIII* (80 mg) in methanol (5 ml) was refluxed with a K_2CO_3 (60 mg) in water (0·9 ml) for 1 h. Methanol was removed *in vacuo*, the product taken into ethyl acetate and the residue after working up was crystallised from ligroin (b.p. 40—60°C) to yield 53 mg of the triol *XVII*, m.p. 156—157°C, $[\alpha]_D^{20}$ +58° (*c* 1·45).

3β-Acetoxy-5β-B-norcholestane-5,6β-diol (*XVIII*)

The ketone *XVI* (240 mg) in acetic acid (5 ml) was hydrogenated over prehydrogenated Adams' catalyst (30 mg) for 8 h. The catalyst was filtered off, acetic acid was removed under reduced pressure, the residue treated with water, and the product taken into ether. Working up and chromatography over silica gel (20 g), elution with benzene–ether (9 : 1) gave after crystallisation from ether 205 mg of the diol *XVIII*, m.p. 140—141°C, $[\alpha]_D^{20}$ +53° (*c* 1·37). For $C_{28}H_{48}O_4$ (448·7) calculated: 74·95% C, 10·78% H; found: 74·96% C, 10·94% H.

3β,6β-Diacetoxy-5β-B-norcholestan-5-ol (*XIX*)

The diol *XVIII* (1 g) was acetylated with acetic anhydride (3 ml) in pyridine (4 ml) for 24 h at room temperature. Usual working up and crystallisation from methanol yielded 910 mg of the diacetate *XIX*, m.p. 107—108°C, $[\alpha]_D^{20}$ +61° (*c* 1·47); IR: 3 595, 1 731, 1 255 cm^{-1}. For $C_{30}H_{50}O_5$ (490·7) calculated: 73·43% C, 10·27% H; found: 73·60% C, 10·22% H.

3β-Acetoxy-6β-methanesulphonyloxy-5β-B-norcholestan-5-ol (*XX*)

A solution of the alcohol *XVIII* (150 mg) in pyridine (2 ml) was treated at 0°C with methanesulphonyl chloride (0·25 ml) and allowed to stand at the same temperature for 2 h. The excess chloride was decomposed with ice, and the product was isolated with ether. Usual working up and crystallisation from ether–ligroin (b.p. 40—60°C) afforded 130 mg of the mesylate *XX*, m.p. 119—121°C, $[\alpha]_D^{20}$ +63° (*c* 1·49). For $C_{29}H_{50}O_6S$ (526·8) calculated: 66·12% C, 9·56% H, 6·08% S; found: 66·01% C, 9·36% H, 5·73% S.

3β-Acetoxy-6β-benzoyloxy-5β-B-norcholestan-5-ol (*XXI*)

A solution of the diol *XVIII* (700 mg) in pyridine (5 ml) was treated with benzoyl chloride (0·7 ml) and set aside at room temperature for 20 h. The reaction mixture was decomposed with ice, and

the product taken into ether. The ethereal solution was worked up, evaporated, and the residue was chromatographed over silica gel (50 g) in ligroin (b.p. 40—60°C)–acetone (30 : 1). The corresponding fractions were combined and evaporated to yield 740 mg of the benzoate *XXI*, $[\alpha]_D^{20}$ +56° (*c* 1·57); the sample resisted all attempts at crystallisation. For $C_{35}H_{52}O_5$ (552·7) calculated: 76·04% C, 9·48% H; found: 75·83% C, 9·27% H.

6β-Benzoyloxy-5β-B-norcholestane-3β,5-diol (*XXII*)

The acetate *XXI* (900 mg) in chloroform (17 ml) and methanol (50 ml) was treated with conc. hydrochloric acid (1 ml) and allowed to stand at 20°C for 60 h. Solvents were removed under reduced pressure, the product taken into ether, the ethereal solution was washed with a $NaHCO_3$ solution, water, dried and evaporated. The diol *XXII* (860 mg) which was pure on thin-layer chromatography resisted all attempts at crystallisation; $[\alpha]_D^{20}$ +54° (*c* 2·70). For $C_{33}H_{50}O_4$ (510·7) calculated: 77·60% C, 9·87% H; found: 77·51% C, 9·61% H.

5,6β-Dihydroxy-5β-B-norcholestan-3-one (*XXIII*)

The benzoate *XXV* (600 mg) in methanol (20 ml) was treated with a KOH (700 mg) in methanol (30 ml) and allowed to stand at 20°C for 6 min. The reaction mixture was diluted with water, and the product taken into ether. The ethereal solution was worked up, evaporated, and the residue was crystallised from methanol to give 520 gm of the diol *XXIII*, m.p. 203—205°C, $[\alpha]_D^{20}$ +15°(*c* 1·20); IR: 3 610, 1 722, 1 090 cm^{-1}. For $C_{26}H_{44}O_3$ (404·6) calculated: 77·18% C, 10·96% H; found: 77·18% C, 10·90% H.

5-Hydroxy-6β-acetoxy-5β-B-norcholestan-3-one (*XXIV*)

The diol *XXIII* (50 mg) in pyridine (0·4 ml) was acetylated with acetic anhydride (0·2 ml) at room temperature for 20 h. Usual working up and crystallisation from methanol gave 35 mg of the acetate *XXIV*, m.p. 195—196°C, $[\alpha]_D^{20}$ −10° (*c* 1·42). For $C_{28}H_{46}O_4$ (446·6) calculated: 75·29% C, 10·38% H; found: 75·09% C, 10·22% H.

5-Hydroxy-6β-benzoyloxy-5β-B-norcholestan-3-one (*XXV*)

The diol *XXII* (820 mg) in acetone (35 ml) was treated with excess Jones' reagent (1·5 ml) and stirred at room temperature for 7 min. After addition of methanol and water the product was extracted with ether, the ethereal solution was worked up, and evaporated. The residue was chromatographed on a silica gel column in ligroin (b.p. 40—60°C–acetone (19 : 1). Working up and crystallisation from methanol yielded 580 mg of the ketone *XXV*, m.p. 63—65°C, $[\alpha]_D^{20}$ +20° (*c* 1·54); IR: 3 580, 1 721, 1 274 cm^{-1}. For $C_{33}H_{48}O_4$ (508·7) calculated: 77·90% C, 9·51% H; found: 77·71% C, 9·47% H.

6β-Hydroxy-B-norcholest-4-en-3-one (*XXVI*)

a) The diol *XXIII* (160 mg) in acetic acid (6 ml) was heated to 100°C under nitrogen in a sealed tube for 3 h. The reaction mixture was diluted with water the product was isolated with ether, the ethereal solution was worked up, and evaporated. The residue was chromatographed over silica gel (20 g) in benzene–ether (9 : 1) to yield after working up and crystallisation from ligrion (b.p. 40—60°C) 110 mg of the ketone *XXVI*, m.p. 174—175°C, $[\alpha]_D^{20}$ −13° (*c* 1·23), identical with the authentic[4] compound. *b*) A solution of the acetate *XXVII* (100 mg) in methanol (30 ml) was treated with $KHCO_3$ (150 mg) in water (6 ml) and kept at 35°C for 48 h. The reaction

mixture was diluted with water, the product isolated with ether and after working up and evaporation, the residue was chromatographed on a silica gel column in benzene–ether (9 : 1). Combination and evaporation of the corresponding fractions followed by crystallisation from ligroin (b.p. 40—60°C) afforded 65 mg of the alcohol *XXVI*, m.p. 174—176°C, $[\alpha]_D^{20}$ −12° (*c* 1·01).

6β-Acetoxy-B-norcholest-4-en-3-one (*XXVII*)

A solution of the acetate *XXIV* (35 mg) in acetic acid (2 ml) was heated to 100°C in a sealed tube under nitrogen for 5 h. The product was isolated similarly as given in the foregoing experiment under *a*) and chromatographed over silice gel (4 g) in ligroin (b.p. 40—60°C)–acetone (19 : 1). The corresponding fractions were combined, evaporated, and the product crystallised from methanol–water to yield 25 mg of the acetate *XXVII*, m.p. 85—86°C, $[\alpha]_D^{20}$ +66° (*c* 1·28). For $C_{28}H_{44}O_3$ (428·6) calculated: 78·45% C, 10·35% H; found: 78·51% C, 10·18% H.

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

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