SYNTHESIS OF SOME UNSATURATED 19a-HOMOCHOLESTANE DERIVATIVES*

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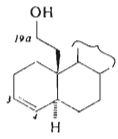
A synthesis of unsaturated alcohols *I*, *II*–*VI* is described. The 3,4-unsaturated derivative *I* was prepared in three steps from the mesylate *VIII* which by elimination of methanesulfonic acid afforded a mixture of olefins *IX* yielding two bromo epoxides *XII* and *XIII* on treatment with hypobromous acid. Zinc reduction of the compound *XIII* gave the hydroxy olefin *I*. In the synthesis of the derivative *IV* inversion of configuration at $C_{(3)}$ (formally *II*→*IV*) was performed in the following manner: reaction of the hypobromous acid with *III* gave the cyclic ether *XV* which after saponification and oxidation was converted into the ketone *XVIII* and the latter was reduced with lithium aluminum hydride to yield a mixture with prepondering equatorial alcohol *XX*. This compound was acetylated and reduced with zinc to give *IV*. The 3-epimeric 10β-vinylalcohols *V* and *VI* were obtained by reduction of the ketone *XXVII*.

For a study dealing with neighboring group participation in electrophilic additions and with participation of the double bond in solvolysis of mesylates we needed a series of unsaturated steroid alcohols *I*, *II*, *IV*–*VI* (Scheme 1). The hydroxy derivative *II* is a known compound[1], syntheses of the remaining four compounds are reported in the present paper.

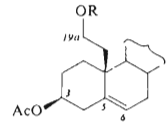
The 3,4-unsaturated alcohol *I* was prepared as follows. On treatment with boiling collidine, the mesylate[1] *VIII* afforded a mixture of isomeric olefins *IX* (Scheme 2) separable with difficulty. Only the 2,3-isomer could be isolated in pure condition[1]. However, addition of hypobromous acid to this mixture proceeds in the both isomers with $6(O)^n$ participation of the methoxyl group in the course of cleavage of the α-bromonium ions *X* and *XI* and gives a relatively easily separable mixture of isomeric bromo epoxides *XII* and *XIII* (in a ratio of 4 : 1). Reduction of the minor bromo epoxide *XIII* with zinc in boiling acetic acid led to the desired 3,4-unsaturated alcohol *I* in a good yield.

In the synthesis of the 3α-acetoxy derivative *IV* from the available 3β-acetoxy derivative *III*, inversion of configuration on $C_{(3)}$ is the key problem. Formally it is a conversion of *II* into *IV*. A nucleophilic substitution of the corresponding 3β-mesyloxy derivative is not feasible since participation of the 5,6-double bond

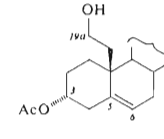
* Part CCXCIV in the series On Steroids: Part CCXCIII: This Journal *48*, 3589 (1983).



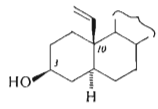
I



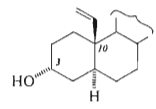
II, R = H
III, R = CH_3



IV

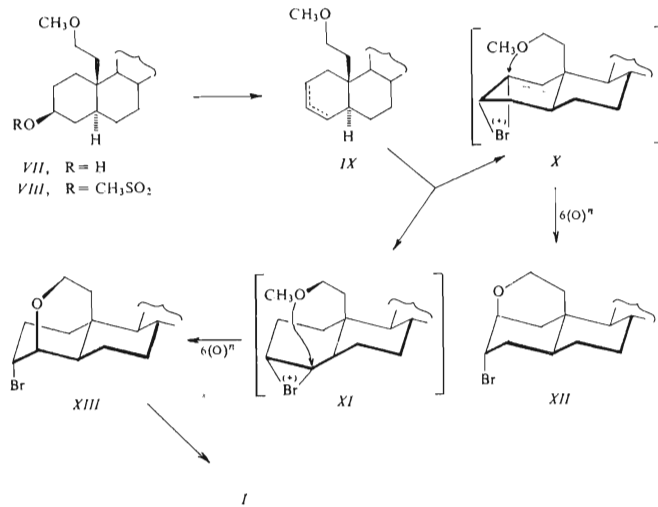


V



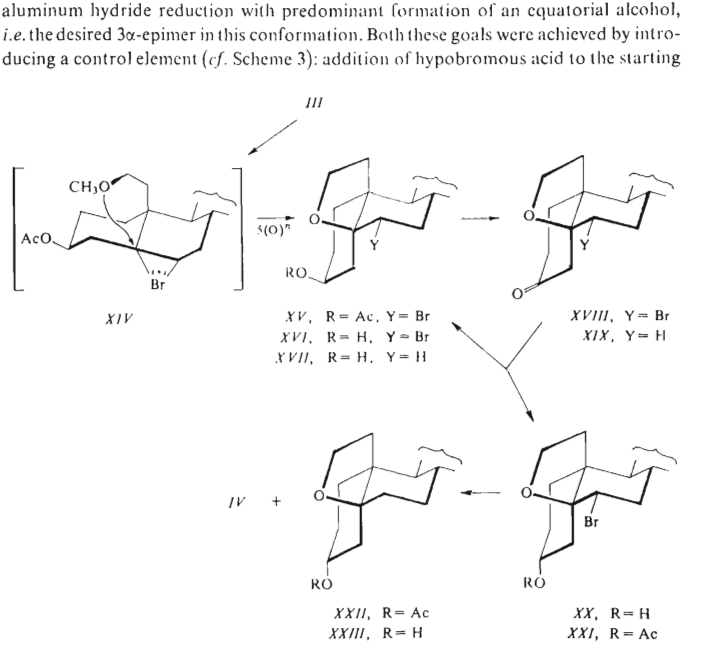
VI

SCHEME 1



SCHEME 2

would give rise to a 3,5-cyclosteroid. Also oxidation of the corresponding 3β-alcohol to a ketone followed by reduction did not seem promising owing to presence of the 5,6-double bond. We found a solution in the following procedure. First, it was necessary to protect the 5,6-double bond, then convert the chair conformation of A-ring in which the 3β-substituent is equatorial, into another chair in which it would be axial. After oxidation to a ketone, the latter should undergo lithium aluminum hydride reduction with predominant formation of an equatorial alcohol, *i.e.* the desired 3α-epimer in this conformation. Both these goals were achieved by introducing a control element (*cf.* Scheme 3): addition of hypobromous acid to the starting

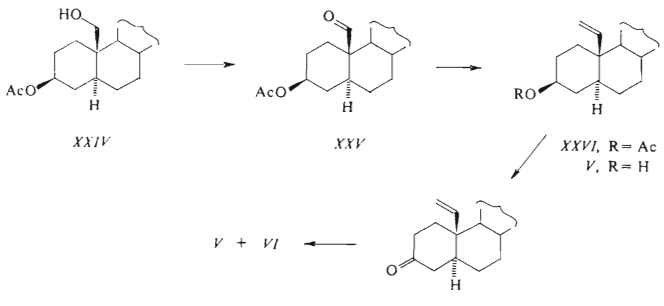


SCHEME 3

3β-acetoxy-5,6-unsaturated methyl ether *III* proceeds with $5(0)^n$ participation in the course of cleavage of the 5α,6α-bromonium ion *XIV* and affords in a good yield the bromo epoxide[1] *XV* as the major product. The acetate group in the latter was removed by treatment with lithium aluminum hydride to give the alcohol *XVI*. In this manner, protection of the double bond and conversion of the A-ring into

the second chair conformation with a 3β-axial group was achieved in one step. Oxidation of the compound *XVI* to the ketone *XVIII* followed by lithium aluminum hydride reduction in ether furnished a mixture of epimeric alcohols *XVI* and *XX* in a 46 : 54 ratio. The undesired 3β-alcohol *XVI* was recycled. When the alcohol *XX* was acetylated and the acetate *XXI* was reduced in usual manner with zinc powder in boiling acetic acid, two products were obtained. The major product (67%) was the saturated epoxide *XXII* resulting from reductive removal of the bromine atom only and the minor product (25%) was the expected unsaturated alcohol *IV*. The adverse course of the reduction of the 3α-derivative *XXI* compared with its 3β-epimer *XV* (which under identical conditions gives the unsaturated alcohol *II* in a fairly smooth reaction) may be attributed to diequatorial arrangement of $C_{(6)}$—Br and $C_{(5)}$—O bonds and to concomitant effect of the 3-acetoxy group. In the 3β-acetate *XV* opening of the epoxide ring is accompanied by removal of a 1,3-*syn*-diaxial interaction whereas in the 3α-epimer *XXI* this effect is absent. Despite the modest yield in the last step (*XXI*→*IV*), the procedure may be considered as preparatively successful. The 5β,19a-epoxide bridge plays not only a role of a control element[2-4] in the reduction of the 3-oxo group and as a protecting group of the 5,6-double bond, but is also a part of a two-step conversion of the 19a-methoxyl to a hydroxy group[5]. It thus fulfils three functions simultaneously.

The structure of the undesired product *XXII* was established by chemical correlation. Reduction of the bromo epoxide *XVI* with tributyltin hydride gave the hydroxy epoxide *XVII* which on oxidation with chromium trioxide in aqueous acetone in the presence of sulfuric acid (Jones' reagent) afforded the epoxy ketone *XIX*. The same epoxy ketone was prepared from the acetoxy epoxide in question (*XXII*) *via* the alcohol *XXIII*.



XXIV *XXV* *XXVI*, R = Ac; *V*, R = H *XXVII*

SCHEME 4

The 3-epimeric 10β-vinyl alcohols *V* and *VI* (Scheme 4) were prepared from the known[6] 5α-cholestane-3β-19-diol 3-monoacetate (*XXIV*). Oxidation of the alcohol *XXIV* gave the aldehyde *XXV* which on Wittig reaction yielded the 3β-acetoxy--10β-vinyl derivative *XXVI* contaminated by alcohol *V* arising probably by saponification during the workup. It also contains some unreacted aldehyde *XXV* and its saponification product. The crude product was therefore acetylated, filtered through aluminum oxide, and crystallized to yield pure acetate *XXVI*. Reduction of the acetate *XXVI* with lithium aluminum hydride provided 3β-hydroxy-10β-vinyl derivative *V* which was converted to the ketone *XXVII* on oxidation with Jones' reagent. Reduction of this ketone with lithium tri-sec-butylborohydride (L-Selectride) led in a good yield to a mixture of epimeric alcohols *V* and *VI* in a 2 : 3 ratio. The yield of the axial 3α-alcohol *VI* is lower when compared with the reduction of 5α-cholestan-3-one[7] which fact is obviously due to greater steric hindrance to the approach of the reagent from the β-site of the ketone *XXVII* caused by the 10β-vinyl group.

EXPERIMENTAL

Melting points were determined on a Kofler block. Analytical samples were dried at 50°C/26 Pa (0·2 Torr). Optical measurements were carried out in chloroform with an error of 3°. 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 Tesla BS 476 instrument (60 MHz) in deuteriochloroform at 30°C with tetramethylsilane as internal reference. Chemical shifts are given in ppm. Apparent coupling constants were obtained from the first order analysis. The mass spectra were recorded on a Jeol JMS D-100 spectrometer operating at 75 eV. The samples were introduced using a direct inlet at lowest temperature enabling evaporation. The elemental composition of ions were determined by accurate mass measurements. The identity of the 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, a 5% aqueous potassium hydrogen carbonate solution, water, drying with sodium sulfate and and evaporation of the solvent *in vacuo*.

19-Homo-5α-cholest-3-en-19a-ol (*I*)

The methoxy derivative *XIII* (200 mg) was dissolved in a mixture of dioxane (1 ml) and acetic acid (4 ml) and to the boiling solution was added powdered zinc (1·5 g) in several portions in the course of 10 min. The inorganic material was filtered off and washed with a hot mixture of acetic acid and acetone (2 : 1). Water was added to a boiling filtrate and the solution was set aside overnight. The crystals (118 mg) were collected by suction and recrystallized from aqueous acetic acid to yield the pure alcohol *I* (89 mg), m.p. 121—122°C, $[\alpha]_D^{20}$ + 50° (*c* 1·4). ^{1}H NMR spectrum: 0·68 (3 H, s, 18-H), 3·80 (2 H, m, W = 30 Hz, 19a-H), 5·45 (2 H, m, W = 40 Hz, 3-H and 4-H). IR spectrum: 1 012, 1 649, 3 018, 3 340, 3 627 cm^{-1}. For $C_{28}H_{48}O$ (400·7) calculated: 80·93% C, 12·07% H; found: 80·99% C, 12·20% H.

19-Homo-5-cholestene-3α,19a-diol 3-Monoacetate (*IV*)

The polar zone after isolation of *XXII* was eluted and the filtrate evaporated to yield the oily *IV*

(54 mg), $[\alpha]_D^{20}$ −12° (*c* 5·4). ^{1}H NMR spectrum: 0·70 (3 H, s, 18-H), 1·98 (3 H, s, CH_3CO_2), 3·68 (2 H, m, W = 30 Hz, 19a-H), 4·98 (1 H, m, W = 12 Hz, 3β-H), 5·43 (1 H, W = 11 Hz, 6-H). For $C_{30}H_{50}O_3$ (458·7) calculated: 78·55% C, 10·99% H; found: 78·40% C, 11·33% H.

19-Nor-10β-vinyl-5α-cholestan-3β-ol (*V*)

a) *From* 19-*nor*-10β-*vinyl*-5α-*cholestan*-3β-*ol* 3-*acetate* (XXVI): The acetate *XXVI* (1 g) was dissolved in ether (50 ml) and treated with lithium aluminum hydride (100 mg) at room temperature for 1 h. The mixture was decomposed with water, diluted with ether and a 5% aqueous hydrochloric acid solution and the ethereal phase was worked up as usual. The residue was crystallized from aqueous acetone to yield the alcohol *V* (760 mg), m.p. 122—123°C, $[\alpha]_D^{20}$ +57° (*c* 1·6). ^{1}H NMR spectrum: 0·53 (3 H, s, 18-H), 3·62 (1 H, m, W = 30 Hz, 3α-H). IR spectrum: 920, 1 007, 1 414, 1 635, 3 080, 3 350, 3 625 cm^{-1}. For $C_{28}H_{48}O$ (400·7) calculated: 83·93% C, 12·07% H; found: 83·70% C, 12·10% H.

b) *From* 19-*nor*-10β-*vinyl*-5α-*cholestan*-3-*one* (XXVII): The polar fraction after isolation of *VI* was evaporated to yield the alcohol *V* (95 mg), m.p. 123—124°C, identical with the compound prepared in the previous experiment.

19-Nor-10β-vinyl-5α-cholestan-3α-ol (*VI*)

The ketone *XXVII* (300 mg) was dissolved in tetrahydrofuran (10 ml), a 1 mol l^{-1} solution of lithium tri-sec-butylborohydride in tetrahydrofuran (1 ml) was added at −45°C dropwise while stirring and the stirring was continued for 2 h. The temperature rised during this time from −45°C to 0°C. The mixture was decomposed with water, a solution of potassium hydroxide (200 mg) in water (2 ml) was added and the mixture was stirred with a 30% aqueous solution of hydrogen peroxide (2 ml) at 60°C for 2 h. The mixture was cooled, eluted with ether and water and the ethereal layer was worked up as usual. The residue was chromatographed on a column of silica gel (30 g) using a mixture of light petroleum, benzene and ether (85 : 10 : 5) to yield the alcohol *VI* (145 mg) m.p. 159—161°C (aqueous acetone), $[\alpha]_D^{20}$ +60°(*c* 1·6). ^{1}H NMR spectrum: 0·55 (3 h, s, 18-H), 3·98 (1 H, m, W = 14 Hz, 3β-H). For $C_{28}H_{48}O$ (400·7) calculated: 83·93% C, 12·07% H; found: 83·74% C, 12·18% H.

3α-Bromo-2β,19a-epoxy-19-homo-5α-cholestane (*XII*)

The mesylate[1] *VII* (15 ml) was refluxed in collidine (15 ml) for 1 h, the solvent was evaporated *in vacuo*, the residue was treated with ether and 5% aqueous hydrochloric acid and the ethereal layer was worked up as usual to yield the crude mixture of isomeric olefins *IX* (960 mg). The crude product was dissolved in dioxane (50 ml) and treated with a 10% aqueous perchloric acid solution (5 ml) and N-bromoacetamide (400 mg) at room temperature for 1 h. The solution was diluted with ether and water, the ethereal phase was washed with water, a 5% aqueous potassium hydrogen carbonate solution, a 5% sodium thiosulfate solution, water, dried, and the solvent was evaporated. The residue was chromatographed on a column of silica gel (90 g) using a mixture of light petroleum and benzene (80 : 20). The lipophilic fraction was evaporated to yield the compound *XII* (775 mg), m.p. 102—103°C identical with an authentic sample[1]. IR spectrum: 1 071 cm^{-1}.

3α-Bromo-4β,19a-epoxy-19-homo-5α-cholestane (*XIII*)

The polar fraction after isolation of *XII* was evaporated to yield *XIII* (146 mg), m.p. 137—138°C (acetone, methanol, water), $[\alpha]_D^{20}$ +22° (*c* 2·3). ^{1}H NMR spectrum: 0·65 (3 H, s, 18-H), 3·74

(1 H, brd s, $W_{1/2}$ = 6·8 Hz, 4α-H), 3·97 (3 H, m, 19a-H), 4·54 (1 H, m, $W_{1/2}$ = 10·4 Hz, 3β-H). IR spectrum: 1 071 cm^{-1}. For $C_{28}H_{47}BrO$ (479·6) calculated: 70·12% C, 9·88% H, 16·66% Br; found: 70·08% C, 9·96% H, 16·70% Br.

6α-Bromo-5,19a-Epoxy-19-homo-5β-cholestan-3β-ol (*XVI*)

a) *From* 6α-*bromo*-5,19a-*epoxy*-19-*homo*-5β-*cholestan*-3β-*ol* 3-*acetate* (XV): The acetate[1] *XV* (1 g) was dissolved in ether (100 ml) and reduced with lithium aluminum hydride (200 mg) at room temperature for 30 min. The mixture was decomposed with water, diluted with ether and 5% aqueous hydrochloric acid and the ethereal phase was worked up as usual. The residue was crystallized from aqueous acetone to yield *XVI* (720 mg), m.p. 164—165°C. IR spectrum: 908, 3 530 cm^{-1}. For $C_{28}H_{47}BrO_2$ (495·6) calculated: 67·86% C, 9·56% H, 16·12% Br; found: 67·64% C, 9·71% H, 16·26% Br.

b) *From* 6α-*bromo*-5,19a-*epoxy*-19-*homo*-5β-*cholestan*-3-*one* (XVIII): The ketone *XVIII* (800 mg) in ether (100 ml) was reduced with lithium aluminum hydride (200 mg) at room temperature for 15 min. The mixture was decomposed with water and worked up as in the previous experiment. The residue was chromatographed on a column of silica gel (40 g) with a mixture of light petroleum, ether and acetone (88 : 10 : 2). The corresponding lipophilic fraction was evaporated to yield *XVI* (250 mg), m.p. 164—165°C identical with the compound prepared in the previous experiment.

5,19a-Epoxy-19-homo-5β-cholestan-3β-ol (*XVII*)

The bromo derivative *XVI* (45 mg) in benzene (5 ml) was refluxed for 3 h with a benzene solution of tributyltin hydride (0·3 ml, 0·20 mg/ml) in the presence of catalytic amount (*c.* 10 mg) of 2,2'-azobis(2-methylpropionitrile) added in five portions. The solution was diluted with ether and washed with water, dried and evaporated. The residue was crystallized from aqueous acetone to afford *XVII* (28 mg) m.p. 103—105°C, $[\alpha]_D^{20}$ +47° (*c* 2·1). IR spectrum: 3 508 cm^{-1}. For $C_{28}H_{48}O_2$ (416·7) calculated: 80·71% C, 11·61% H; found: 80·63% C, 11·51% H.

6α-Bromo-5,19a-epoxy-19-homo-5β-cholestan-3-one (*XVIII*)

The alcohol *XVII* (1 g) was dissolved in a mixture of acetone (20 ml) and benzene (10 ml) and treated with Jones' reagent (3 ml) at 0°C for 10 min. The excess of the reagent was decomposed with methanol (5 min at 0°C), the mixture was diluted with ether and water and the ethereal layer was washed with water, a 5% aqueous potassium hydrogen carbonate solution, water, dried and the solvent was evaporated. The residue was crystallized from a mixture of acetone, methanol and water to yield the ketone *XVIII* (900 mg), m.p. 139—140°C. IR spectrum: 908, 1 722 cm^{-1}. For $C_{48}H_{45}BrO_2$ (493·6) calculated: 68·14% C, 9·19% H, 16·19% Br; found: 68·03% C, 9·22% H, 16·37% Br.

5,19a-Epoxy-19a-homo-5β-cholestan-3-one (*XIX*)

a) *From* 5,19a-*epoxy*-19-*homo*-5β-*cholestan*-3β-*ol* (XVII): the alcohol *XVII* (20 mg) was dissolved in acetone (5 ml) and treated with Jones' reagent at room temperature for 5 min. The excess of the reagent was decomposed with methanol, the mixture was diluted with ether and water and the etheral phase was worked up as usual. The residue was crystallized from aqueous acetone to yield the ketone *XIX* (12 mg), m.p. 103—104°C, $[\alpha]_D^{20}$ +19° (*c* 1·8). IR spectrum: 1 402, 1 722 cm^{-1}. For $C_{28}H_{46}O_2$ (414·7) calculated: 81·10% C, 11·18% H; found: 80·38% C, 11·43% H.

b) *From* 5,19a-*epoxy*-19a-*homo*-5β-*cholestan*-3α-*ol* (XXIII): the alcohol *XXIII* (50 mg) in a mixture of acetone (3 ml) and benzene (1 ml) was treated with Jones' reagent at 0°C for 10 min. The mixture was worked up as given in the previous experiment. The residue was crystallized from aqueous acetone to give the ketone *XIX* (28 mg), m.p. 102—103°C identical with the compound prepared under *a*.

6α-Bromo-5,19-epoxy-19-homo-5β-cholestan-3α-ol (*XX*)

Elution with a mixture of light petroleum, ether and acetone (86 : 10 : 4) after isolation of *XVI* furnished a polar fraction. This fraction was evaporated to yield the oily compound *XX* (295 mg), $[\alpha]_D^{20}$ +5° (*c* 5·8). For $C_{28}H_{47}BrO_2$ (495·6) calculated: 67·86% C, 9·56% H, 16·12% Br; found: 67·69% C, 9·62% H, 16·01% Br.

6α-Bromo-5,19a-epoxy-19-homo-5β-cholestan-3α-ol 3-Acetate (*XXI*)

The alcohol *XX* (280 mg) was dissolved in pyridine (3 ml) and treated with acetic anhydride (1·2 ml) at room temperature overnight. The mixture was decomposed with ice and water, the product was extracted with ether and the ethereal layer was worked up as usual to yield the oily acetate *XXI* (265 mg), $[\alpha]_D^{20}$ +3° (*c* 3·4). ^{1}H NMR spectrum: 0·65 (3 H, s, 19-H), 2·00 (3 H, s, CH_3CO_2), 4·00 (2 H, m, W = 20 Hz, 19a-H), 4·32 (1 H, m, W = 25 Hz, 6β-H), 4·95 (1 H, m, W = 30 Hz, 3β-H). For $C_{30}H_{49}BrO_3$ (537·6) calculated: 67·02% C, 9·19% H, 14·86% Br; found: 66·77% C, 9·21% H, 14·72% Br.

5,19a-Epoxy-19a-homo-5β-cholestan-3α-ol 3-Acetate (*XXII*)

The bromoepoxide *XXI* (250 mg) was dissolved in a mixture of dioxane (1 ml), acetic acid (4 ml) and methanol (0·5 ml) and refluxed with powdered zinc (1·5 g, added in ten portions) while stirring for 10 min. The inorganic material was filtered off, washed with a mixture of acetic acid and acetone (3 : 1), the filtrate was cooled, diluted with ether and water, the ethereal phase was washed with water, a 5% aqueous potassium hydrogen carbonate solution, water, dried and the solvent was evaporated. The residue was chromatographed on three preparative silica gel plates (20 × 20 cm) using a mixture of light petroleum, ether and acetone (80 : 10 : 10). The lipophilic zone was collected, eluted with ether and the eluate was evaporated to afford the oily acetate *XXII* 144 mg, $[\alpha]_D^{20}$ +26° (*c* 1·8). ^{1}H NMR spectrum: 0·63 (3 H, s, 18-H), 2·00 (3 H, s, CH_3CO_2), 3·92 (2 H, m, W = 20 Hz, 19a-H), 5·00 (1 H, m, W = 30 Hz, 3β-H). For $C_{30}H_{50}O_3$ (458·7) calculated: 78·55% C, 10·99% H; found: 78·34% C, 11·26% H.

5,19a-Epoxy-19a-homo-5β-cholestan-3α-ol (*XXIII*)

The acetate *XXII* (140 mg) was dissolved in ether (5 ml) and treated with lithium aluminum hydride (50 mg) at room temperature for 1 h. The mixture was decomposed with water, diluted with ether and a 5% aqueous hydrochloric acid solution and the ethereal layer was worked up as usual. The residue was crystallized from aqueous acetone to yield the alcohol *XXIII* (92 mg), m.p. 157—158°C, $[\alpha]_D^{20}$ +41° (*c* 1·6). IR spectrum: 3 627 cm^{-1}. For $C_{28}H_{48}O_2$ (416·7) calculated: 80·71% C, 11·61% H; found: 80·81% C, 11·53% H.

3β-Acetoxy-5α-cholestan-19-al (*XXV*)

The alcohol[6] (*XXIV*) (1·2 g) was dissolved in acetone (30 ml) and treated with Jones' reagent at 0°C for 5 min. The excess of the reagent was decomposed with methanol (5 min at 0°C) the mixture was diluted with ether and water, the ethereal layer was washed with water, a 5% aqueous

potassium hydrogen carbonate solution, water, dried and the solvent was evaporated. The residue was crystallized from a mixture of acetone, methanol and water to yield the aldehyde *XXV* (820 mg), m.p. 94–97°C (dec.), $[\alpha]_D^{20}$ (*c* 1·8). ^{1}H NMR spectrum: 0·57 (3 H, s, 18-H), 1·98 (3H, s, CH_3CO_2), 4·73 (1 H, m, W = 30 Hz, 3α-H), 10·00 (1 H, s, 19-H). For $C_{29}H_{48}O_3$ (444·7) calculated: 78·33% C, 10·88% H; found: 78·11% C, 10·94% H.

19-Nor-10β-vinyl-5α-cholestan-3β-ol 3-Acetate (*XXVI*)

Sodium hydride (150 mg) was dissolved in dimethyl sulfoxide (7 ml) with stirring and heating at 65°C for 2 h. Triphenylphosphonium iodide (1 g) was then added at room temperature and the mixture was stirred at room temperature for 30 min. A solution of the aldehyde *XXV* (1 g) in tetrahydrofuran (7 ml) was added and the mixture was stirred at 65°C for 2 h. The mixture was cooled, diluted with ether and water and the ethereal phase was worked up as usual. The residue was dissolved in pyridine (10 ml) and treated with acetic anhydride (3 ml) and room temperature overnight. The mixture was decomposed with ice and water, the product was taken up into ether and the ethereal layer was worked up as usual. The residue was dissolved in a mixture of light petroleum and benzene (9 : 1) and filtered through a column of aluminum oxide. The filtrate was evaporated and the residue was crystallized from a mixture of acetone, methanol and water to afford the acetate *XXVI* (770 mg), m.p. 105–106°C, $[\alpha]_D^{20}$ + 40° (*c* 1·9). ^{1}H NMR spectrum: 0·55 (3 H, s, 18-H), 1·97 (3 H, s, CH_3CO_2), 4·73 (1 H, m, W = 30 Hz, 3α-H). IR spectrum: 920, 984, 1 248, 1 414, 1 635, 1 735, 3 080 cm^{-1}. For $C_{30}H_{50}O_2$ (442·7) calculated: 81·39% C, 11·38% H; found: 81·17% C, 11·53% H.

19-Nor-10β-vinyl-5α-cholestan-3-one (*XXVII*)

The alcohol *V* (330 mg) was dissolved in acetone (20 ml) and treated with Jones' reagent at room temperature for 5 min. The excess of the reagent was decomposed with methanol (5 min at room temperature), the mixture was diluted with ether and water, the ethereal layer was washed with water, a 5% aqueous potassium hydrogen carbonate solution, water, dried and the solvent was evaporated. The residue was crystallized from a mixture of acetone, methanol and water to yield the ketone *XXVII* (190 mg), m.p. 105–107°C, $[\alpha]_D^{20}$ + 89° (*c* 2·1). IR spectrum: 922, 1 007, 1 416, 1 635, 1 719, 3 080 cm^{-1}. For $C_{28}H_{46}O$ (398·7) calculated: 84·36% C, 11·63% H; found: 84·10% C, 11·78% H.

The analyses were carried out in the analytical laboratory of this Institute (head Dr J. Horáček). The IR *spectra were recorded by Mrs K. Matoušková and interpreted by Dr S. Vašíčková. The* ^{1}H NMR *spectra were recorded by Mrs J. Jelinková and M. Snopková. The mass spectra were recorded by Dr Fr. Tureček, The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Prague 2.*

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