A NEW TYPE OF A-HOMO-B-NORCHOLESTANE DERIVATIVES*

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5-Bromo-6β-chloro-5α-cholestan-3β-ol (*I*) undergoes solvolysis to yield products of Westphalen rearrangement one of them (*XXIX*) undergoing further rearrangement to the A-homo-B-nor-system *V*. The reaction course was established by the use of suitably labeled substrates. The structures of the products and positions of the labels were determined by chemical transformations and physicochemical methods (^{1}H, ^{13}C NMR spectra).

In connection with another problem it appeared desirable to furnish an unequivocal structure proof of a product of rearrangement occurring in the course of solvolysis of 5-bromo-6β-chloro-5α-cholestan-3β-ol (*I*). The preparation of the compound *V* was reported[1] (Scheme 1) and its structure was tentatively formulated as *IV*. An analysis of ^{1}H NMR spectrum (200 MHz) of the compound *V* shows now that the double bond is situated in the position 1(10): A signal of an allylic proton was found (2·52 ppm) and its coupling both with the vinyl ($J_{1,2}$ = 2 Hz) and with the 3α-proton ($J_{2,3}$ = 5 Hz) was proved by means of decoupling experiments. Additional evidence for location of the double bond in the A-ring was provided by oxidative cleavage of this bond which was performed indirectly *via* the dihydroxy derivative *VIII*. The latter was obtained from the olefin *V* by treatment with osmium tetroxide. The diol *VIII* was oxidized with periodic acid to give the ketoaldehyde *XII* showing an absorption band of a five-membered ketone (1 749 cm^{-1}). In the mass spectrum of the ketoaldehyde *XII* a prominent peak was found at 141 *m/z* which is presumably due to the fragment *a* (*cf.* Scheme 2) consisting of the rest of the A-ring with $C_{(6)}$ and $C_{(7)}$ atoms. The fragment *a* further loses acetaldehyde being converted into the fragment *b* (96 *m/z*) in way which is compatible with the structures of both the molecular ion and the fragment *a*. This explanation is in accord with the results obtained with the labeled derivatives *VI* and *VII*: the masses of the fragments *a* and *b* in the spectra of the corresponding ketoaldehydes *XIII* and *XIV* demonstrate that the both fragments contain together with the rest of the A-ring, the carbon atoms $C_{(6)}$ and $C_{(7)}$.

The formation of the compound *V* in the solvolysis of the bromo chloride *I* can be

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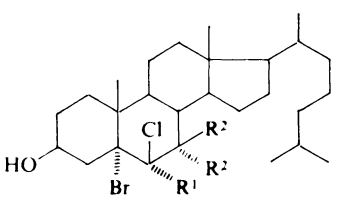
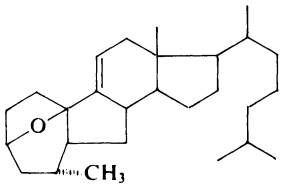
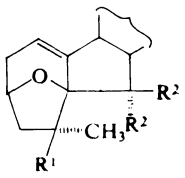
exploined by the following sequence (*cf.* Scheme 3): The first step in the transformation of the compound *I* is a preferential splitting off of the more reactive halo-



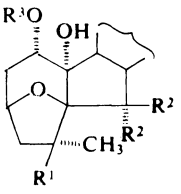
I, $R^1 = H$, $R^2 = H$
II, $R^1 = {}^2H$, $R^2 = H$
III, $R^1 = H$, $R^2 = {}^2H$



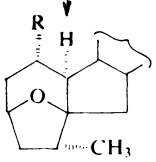
IV



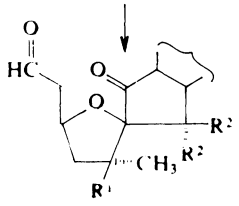
V, $R^1 = H$, $R^2 = H$
VI, $R^1 = {}^2H$, $R^2 = H$
VII, $R^1 = H$, $R^2 = {}^2H$



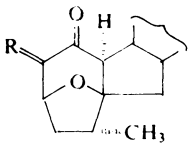
VIII, $R^1 = H$, $R^2 = H$, $R^3 = H$
IX, $R^1 = {}^2H$, $R^2 = H$, $R^3 = H$
X, $R^1 = H$, $R^2 = {}^2H$, $R^3 = H$
XI, $R^1 = H$, $R^2 = H$, $R^3 = CH_3CO$



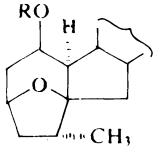
XV, R = OH
XVI, $R = C_6H_5COO$
XVII, $R = CH_3SO_3$
XVIII, R = H



XII, $R^1 = H$, $R^2 = H$
XIII, $R^1 = {}^2H$, $R^2 = H$
XIV $R^1 = H$, $R^2 = {}^2H$



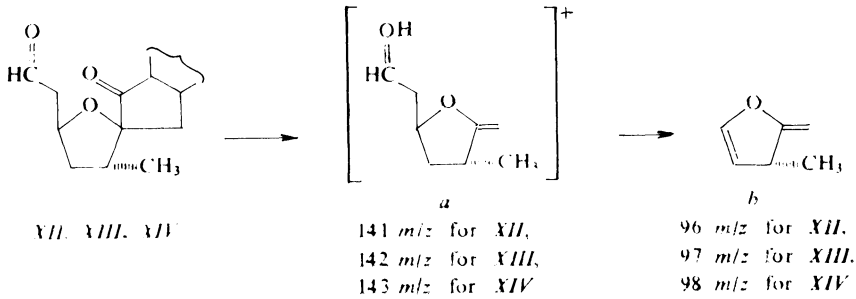
XIX, $R = H_2$
XX, $R = C_6H_5CH$



XXI R = H
XXII $R = C_6H_5CO$

SCHEME 1

gen, *i.e.* bromine located at the tertiary carbon atom[2]. Strong diaxial interaction between the $C_{(10)}$-methyl group and the chlorine atom is the driving force of the Westphalen rearrangement[3]. One of the products of this rearrangement, the $\Delta^{1(10)}$-



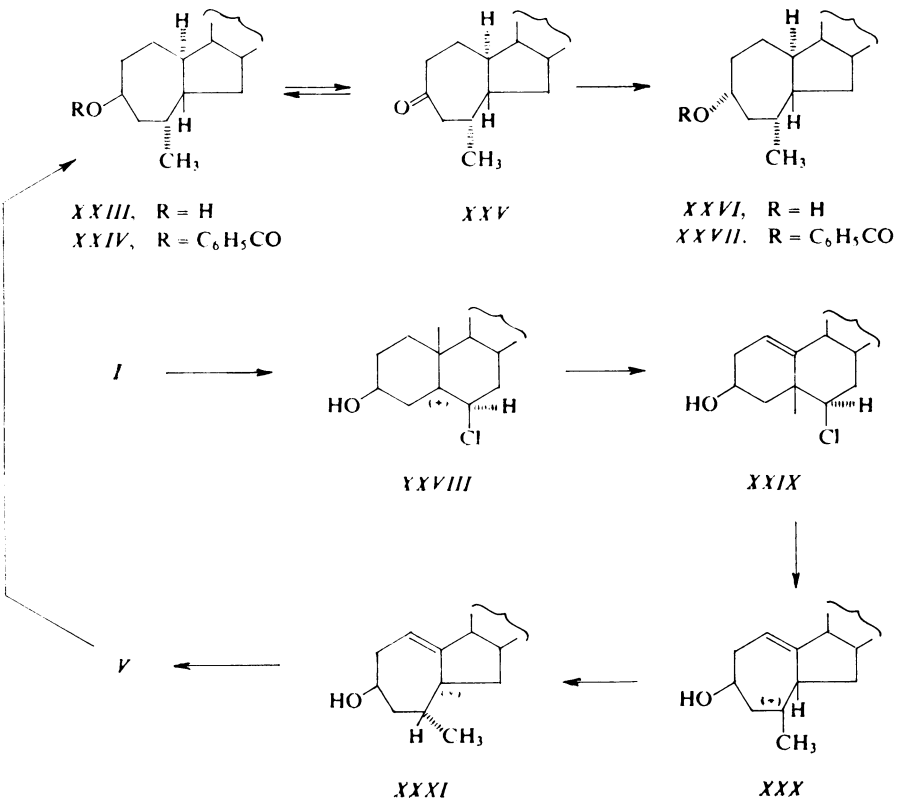
VII, *VIII*, *IX* — *a* — *b*

141 *m/z* for *XII*, 142 *m/z* for *XIII*, 143 *m/z* for *XIV* — 96 *m/z* for *XII*, 97 *m/z* for *XIII*, 98 *m/z* for *XIV*

SCHEME 2

-olefin *XXIX* undergoes further transformation in the reaction medium: One of the two most likely conformations of the B-ring is characterized by the antiperiplanar orientation of the 6β-chlorine atom with respect to the $C_{(5)}$—$C_{(10)}$ bond favoring thus contraction of the B-ring and formation of the carbocation *XXX* during the solvolysis of the chloro derivative *XXIX*. The intramolecular interaction of the positive center with the electron pair of the hydroxyl group is not rewarding since it would provide a product with a four-membered heterocycle. For this reason, the cation suffers a more favorable transformation into the cation *XXXI* which is the direct precursor of the 3β,6-epoxy derivative *V*. This hypothesis was corroborated by means of the labeled substrates *VI* and *VII*. ^{1}H NMR spectrum of the monodeutero derivative *VI*, obtained from the bromo chloride *II*, exerts a singlet of $C_{(19)}$-protons and demonstrates thus a shift of the hydride ion from the 6β into 5β-position. The bromo chloride *III* was converted into the dideutero derivative *VII* and the ^{13}C NMR spectrum of the latter was compared with that of the compound *V* to prove that the both deuterium atoms are situated at the same carbon atom and that the rearrangement remained localized on the carbons $C_{(5)}$ and $C_{(6)}$. The same evidence is provided by the C—^{2}H stretching vibrations region of the IR spectrum containing 3 absorption bands interpretable as a doublet due to symmetric and antisymmetric vibration of the C^2H_2 group with one branch split by Fermi resonance. This finding gives credibility to the above hypothesis postulating the sequence of the rearrangements to be limited only to carbons $C_{(10)}$, $C_{(5)}$ and $C_{(6)}$. These results make it possible to assign configurations at all chirality centers in the molecule of the compound *V*: The configurations on the carbons $C_{(8)}$ and $C_{(9)}$ remain the same as in the parent steroid *I*, the configuration on the $C_{(4a)}$-carbon is given by the orientation of the $C_{(5)}$-hydrogen

in the carbocation *XXX* (the 5β-configuration of the cation *XXX* follows from the Walden inversion in the solvolysis of the 6β-chlorine with rearrangement of the $C_{(5)}$—$C_{(10)}$-bond).



SCHEME 3

Proving the structures involved several addition reactions to the double bond in the compound *V* and structures of the products were determined in the following manner: Hydroboration and subsequent oxidation with hydrogen peroxide gave the hydroxy derivative *XV* in which the IR spectrum demonstrated absence of a hydrogen bond between the OH group and the ether oxygen atom. However, oxidation gave the ketone *XIX* which on reduction yielded the epimeric 1-hydroxy derivative *XXI* with strong intramolecular hydrogen bond (IR absorption at 3 556 cm^{-1}). We can thus assign the 1β-configuration to this compound and 1α,10α-configuration to the product of hydroboration (*XV*). It thus turned out that the reagent approaches the double bond practically exclusively from the α-face.

The 1α-hydroxy derivative *XV* was converted to the methanesulfonate *XVII* and then subjected to treatment with reduction reagents. Whereas zinc powder and potassium iodide[4] led only to elimination to the olefin *V*, refluxing with a solution of lithium aluminum hydride gave rise to a mixture of the olefin *V* and deoxy derivative *XVIII* which was found to be identical with the product of catalytic hydrogenation of the compound *V*. This finding demonstrated that also the catalyst approaches the double bond of the unsaturated 3β,6-epoxy derivative *V* from the α-face.

TABLE I

Characteristic parameters of ^{1}H NMR spectra. The spectra were measured on a Tesla 60 instrument, unless noted otherwise. Tetramethylsilane was used as internal standard, chemical shifts are given in the δ-scale

Compound	1-H	3-H	18-H	19-H[a]	Other signals[b]
V	5·02[c]	4·48[d]	0·65	0·92	—
VI	5·02[c]	4·48[d]	0·65	0·92[e]	—
VII	5·02[c]	4·48[d]	0·65	0·92	—
VIII	3·88[f]	4·31[g]	0·68	0·90	—
XI	4·91[f]	4·37[g]	0·64	0·90	2·02[h]
XV	3·81[i]	4·33[j]	0·68	0·87	—
XVI	5·06[t]	4·44[j]	0·64	0·84	7·47[k], 8·05[k]
XVII	4·72[i]	4·50[j]	0·70	0·90	2·94[l]
XVIII	—	4·25[m]	0·65	0·89	—
XIX	—	4·56[n]	0·66	0·99	—
XX	—	5·24[o]	0·65	1·05	7·34[k]
XXI	3·84[p]	4·47[n]	0·71	[q]	—
XXII	5·42[p]	4·43[n]	0·20[r]	0·86	7·49[k], 8·06[k]
XXIII[s]	—	3·92[t]	0·65	0·90[u]	—
XXIV[s]	—	5·24[t]	0·68	0·93[u]	7·49[k], 8·04[k]
XXV	—	—	0·64	0·90	—
XXVI[s]	—	3·96[v]	0·62	0·90[u]	—
XXVII[s]	—	5·26[w]	0·65	0·92[u]	7·47[k], 8·05[k]

[a] Doublet (J = 6·3 Hz) unless stated otherwise; [b] doublet of $C_{(21)}$-protons (0·90 + 0·01 ppm, J = 6·8 Hz) and doublet of $C_{(26,27)}$-protons (0·85 + 0·01 ppm, J = 6·5 Hz) were observed in all the spectra; [c] multiplet, $W_{1/2}$ = 7 Hz; [d] doublet of doublets, J = 5 and 6 Hz; [e] singlet; [f] doublet of doublets, J = 8 and 10 Hz; [g] doublet of doublets, J = 7 and 9 Hz; [h] singlet ($COCH_3$); [i] doublet of doublets, J = 8 and 17 Hz; [j] triplet, J = 7·5 Hz; [k] multiplet of aromatic protons; [l] singlet (O_2SCH_3); [m] doublet of doublets, J = 5·2 and 9 Hz; [n] doublet of doublets, J = 5 and 10 Hz; [o] broad doublet, J = 6 Hz; [p] doublet of doublets, J = 2·5 and 2·5 Hz; [q] obscured by other signals; [r] after hydrogenation to a hexahydrobenzoyloxy derivative the signal appears at 0·66 ppm again; [s] measured on a Varian instrument (XL200); [t] multiplet W = 25·4 Hz; [u] doublet, J = 6·8 Hz; [v] multiplet, W = 18·0 Hz; [w] multiplet, W = 22·6 Hz.

The products of hydroxylations of olefins *V*–*VII* with osmium tetroxide were formulated as 1α,10α-dihydroxy derivatives *VIII*–*X* merely from analogy with the above described additions. However, the correctness of this assignement is corroborated by ^{1}H NMR spectrum of the acetylated diol (*XI*, Table I), where the $C_{(1)}$-proton shows two strong couplings with the neighboring protons ($J_{1,2\alpha}$ = 10 Hz, $J_{1,2\beta}$ = 8 Hz).

Catalytic hydrogenation of compounds *V* and *XVI* on platinum catalyst provides the tetrahydro derivative *XXIII* (mass spectrometry) containing one secondary hydroxyl group in the molecule. The compound *XXIII* is allotted 5β-configuration on the basis of knowledge[5] of hydrogenolysis mechanism of tertiary allyl ethers on platinum catalyst (the insertion mechanism). The oxidation of the compound *XXIII* yields the ketone *XXV* with typical IR-absorption of a cycloheptanone system (1 705 cm^{-1}). Reduction of this ketone with lithium tri-tert-butoxyaluminum hydride gave a mixture of 3β-hydroxy and 3α-hydroxy derivatives *XXIII* and *XXVI* in a ratio of 1 : 1 and both compounds were subjected to photochemical oxidation in the presence of iodine and lead tetraacetate. No 3β,5-epoxy derivative *XVIII* was found in any case: The starting substances were consumed to give rise to products with the open A-ring.

EXPERIMENTAL

Melting points are determined on a Kofler block and are uncorrected, analytical samples were dried over phosphorus pentoxide (1 kPa) at room temperature for 8 h. Unless noted otherwise, the IR spectra were measured in tetrachloromethane solution, circular dichroism in methanol (Jeol FX 60), specific rotations in chloroform and the NMR spectra in deuteriochloroform (Tesla 60 MHz, Varian XL 200). Identity of the samples obtained by different procedures was corroborated by comparison of their IR spectra and by mixture melting point determinations.

3β,5-Epoxy-4aα-methyl-A-homo-B,19-dinor-5β-cholest-1(10)-ene (*V*)

A solution of the methanesulfonate *XVII* (110 mg) and Sodium iodide (0·4 g) in dimethoxyethane (15 ml) was stirred with zinc powder (2 g) under reflux. After 4 h the inorganic portion was filtered off, washed with chloroform (c. 60 ml) and the filtrate was washed with aqueous solution of sodium thiosulfate and water. The product was purified by chromatography on a thin layer of silica gel (benzene). The major component melts at 135–138°C (53 mg, methanol) and the mixture m.p. with the compound *V* prepared earlier[1] shows no depression. Mass spectrum: 384 (100%, M^+), 383 (33·5%, M – H), 369 (2·3%, M – CH_3), 341 (32·7%, M – C_3H_7), 303 (8·9%, M – – C_5H_5O) *m/z*. ^{13}C NMR spectrum: 152·36, 107·49, 86·74, 77·03, 74·92, 72·97, 56·00, 55·83, 49·66, 44·30, 44·10, 43·05, 40·28, 39·51, 39·19, 36·26, 35·65, 34·31 ($C_{(7)}$-signal) 33·99, 28·42, 27·98, 24·04, 23·84, 22·82, 22·54, 18·76, 18·48, 12·34 ppm.

[4a-^{2}H]-3β,5-Epoxy-4aα-methyl-A-homo-B,19-dinor-5β-cholest-1(10)-ene (*VI*)

A solution of the compound *II* (1·1 g) in tetrahydrofuran (4 ml) was added to a silver perchlorate (0·4 g) solution in water (1 ml) and tetrahydrofuran (2 ml) kept under nitrogen. The mixture was

stirred in darkness at 65°C for 1 h, diluted with c. 100 ml of chloroform, the solution decanted from a precipitate which was then decanted with two additional 50 ml portions of chloroform. The combined chloroform extracts were washed with water, dried over sodium sulfate and the solvent evaporated. The residue was chromatographed on a silica gel (40 g) column, 2% acetone–light petroleum eluted the compound *VI*, m.p. 137–138°C (methanol, 63 mg); mass spectrum: 385 (100%, M^+), 384 (42·8%, M − H), 383 (5·3%, M − 2), 370 (2·9%, M − CH_3), 341 (35·7%, M − $C_3H_6{}^2H$), 303 (8·2%, M − $C_5H_4{}^2HO$) *m/z*. For $C_{27}H_{43}{}^2HO$ (385·6) calculated: 84·09% C, 11·76% H; found: 84·16% C, 11·69% H.

[6,6-^{2}H]-3β,5-Epoxy-4aα-methyl-A-homo-B,19-dinor-5β-cholest-1(10)-ene (*VII*)

Similarly, the compound *III* (2·03 g) gave the substance *VII* (69 mg), m.p. 135–137°C (methanol) Mass spectrum: 386 (100%, M^+), 385 (34·5%, M − H), 384 (10·9%, M − 2), 371 (3·2%, M − − CH_3), 343 (30%, M − C_3H_7), 305 (8·1%, M − C_5H_5O) *m/z*: IR spectrum: 2 105, 2 130, 2 220 (CD_2) cm^{-1}; ^{13}C NMR spectrum: 152·45, 107·51, 86·70, 77·03, 75·43, 73·03, 56·05, 55·92, 49·69, 44·38, 44·14, 42·92, 40·37, 39·56, 39·29, 36·33, 35·69, 34·03, 28·46, 28·03, 24·10, 23·91, 22·81, 22·58, 18·84, 18·50 and 12·38 ppm. For $C_{27}H_{42}{}^2H_2O$ (386·6) calculated: 83·87%, C, 11·99% H; found: 84·13% C, 11·70% H.

[6α-^{2}H]-5-Bromo-6β-chloro-5α-cholestan-3β-ol (*II*)

A solution of [6-^{2}H]-cholesterol (4·2 g) in chloroform (33 ml) was saturated with dry hydrogen chloride at 0°C and treated portionwise with a solution of N-bromoacetamide (1·6 g) in chloroform (33 ml). After 10 min the mixture was filtered, the filtrate washed with water, aqueous potassium hydrogen carbonate solution, dried with sodium sulfate and the solvent removed under reduced pressure. The residue was crystallized from ethyl acetate and methanol to give the compound *II* (4·7 g), m.p. 136–142°C, $[\alpha]_D^{20}$ −56° (*c* 1·1). ^{1}H NMR spectrum was identical with that of the compound *I* except for absence of the signal at 4·62 ppm. For $C_{27}H_{45}{}^2HBrClO$ (503·0) calculated: 64·74% C, 9·42% H; found: 64·53% C, 9·61% H.

[7,7-^{2}H]-5-Bromo-6β-chloro-5α-cholestan-3β-ol (*III*)

[7,7-^{2}H]-Cholesterol[7] was converted to the compound *III* in similar manner. Its ^{1}H NMR spectrum (60 MHz) is identical with that of the compound *I*; IR spectrum: 2 214, 2 106, 2 112 (C^2H_2) cm^{-1}. For $C_{27}H_{44}{}^2H_2BrClO$ (504·0) calculated: 64·33% C, 9·59% H; found: 64·42% C, 9·43% H.

3β,5-Epoxy-4aα-methyl-A-homo-B,19-dinor-5β,10α-cholestan-1α,10-diol (*VIII*)

A solution of the olefin *V* (150 mg) and osmium tetroxide (100 mg) in ether (3 ml) was allowed to react at room temperature for 4 days. The mixture was concentrated, the residue was combined with a solution of sodium hydrogen sulfite (0·5 g) in water (5 ml) and ethanol (20 ml) and heated at reflux temperature for 8 h. The solution was concentrated *in vacuo* diluted with water and the precipitate taken up in ether. After crystallization from light petroleum m.p. 118–120°C (76 mg), $[\alpha]_D^{20}$ +27° (*c* 1·1); mass spectrum: 418 *m/z* (M+). For $C_{27}H_{46}O_3$ (418·6) calculated: 77·46% C, 11 08% H; found: 77·31% C, 11·20% H.

[4aβ-^{2}H]-3β,5-Epoxy-4aα-methyl-A-homo-B,19-dinor-5β,10α-cholestan-1α,10-diol (*IX*)

In similar manner, the compound *VI* (50 mg) was converted to the diol *IX* (47 mg), m.p. 118 to 120°C. Mass spectrum: 419 *m/z* (M^+).

[7,7-^{2}H]-3β,5-Epoxy-4aα-methyl-A-homo-B,19-dinor-5β,10α-cholestan-1α,10-diol (*X*)

Analogously, the compound *VII* (150 mg) was oxidized with osmium tetroxide to yield the diol *X*, m.p. 118–120°C; mass spectrum: 420 *m/z* (M^+).

1α-Acetoxy-3β,5-epoxy-4aα-methyl-A-homo-B,19-dinor-5β,10α-cholestan-10-ol (*XI*)

The diol *VIII* (270 mg) was acetylated with acetic anhydride (0·5 ml) in pyridine (0·5 ml). After 18 h the mixture was diluted with water, the precipitate filtered, washed with water and crystallized from methanol, m.p. 141–143°C, $[\alpha]_D^{20}$ +24° (*c* 0·9). For $C_{29}H_{48}O_4$ (460·7) calculated: 75·61% C, 10·50% H; found: 75·44% C, 10·44% H.

Oxidization of the Diols *VIII*–*X* with Periodic Acid

a) A 10% aqueous periodic acid solution (0·25 ml) was added to a solution of the diol *VIII* (13 mg) in acetone (1 ml). After 1 h the solution was diluted with benzene (c. 20 ml) and washed with an aqueous solution of potassium hydrogen carbonate and water. The benzene solution was concentrated *in vacuo* and applied to a thin layer of silica gel, the plate was developed by light petroleum–ether (10%) and detected by morine in acetone solution. The major product *XII* (8mg) was eluted by ethyl acetate, the solvent removed under reduced pressure and the residue analysed. IR-spectrum: 1 729 and 2 725 (—CHO), 1 749 (cyclopentanone) cm^{-1}; mass spectrum: 416 *m/z* (M^+); $[\alpha]_D^{20}$ +110° (*c* 0·8

b) The same procedure was applied to the diol *IX* to yield the ketoaldehyde *XIII*; mass spectrum: 417 *m/z* (M^+).

c) The same procedure was applied to the diol *X* to give the seco-aldehyde *XIV*; mass spectrum: 418 *m/z* (M^+).

3β,5-Epoxy-4α-methyl-A-homo-B,19-dinor-5β,10α-cholestan-1α-ol (XV)

A saturated solution of lithium aluminum hydride (25 ml) was added in an atmosphere of nitrogen to a stirred solution of the olefin *V* (0·6 g) and børøn trifluoride etherate (2 ml) in ether (15 ml) over 1 h period. Excess reagent was decomposed by several drops of saturated aqueous sodium sulfate solution and the mixture poured on a sodium sulfate column. The product was eluted with ether (100 ml) the solvent evaporated and the residue dissolved in tetrahydrofuran (3 ml). This solution was shaken with hydrogen peroxide (0·3 ml) and sodium hydroxide solution (0·5 ml, 3 N) for 2 h. The mixture was diluted with saturated aqueous solution of sodium chloride (80 ml), the product taken up in ether, washed with water and dried with sodium sulfate. Thin layer chromatography yielded the oily alcohol *XV* (510 mg), $[\alpha]_D^{20}$ +46° (*c* 1·1). Mass spectrum: 402 *m/z* (M^+), 319 *m/z* ($M - C_6H_{11}$). For $C_{27}H_{46}O_2$ (402·6) calculated: 80·54% C, 11·52% H; found: 80·72% C, 11·61% H.

1α-Benzoyloxy-3β,5-epoxy-4aα-methyl-A-homo-B,19-dinor-5β,10α-cholestan (*XVI*)

The hydroxy derivative *XV* (175 mg) was treated with benzoyl chloride (0·2 ml) in pyridine (0·2 ml) for 18 h. The mixture was poured into hot water (10 ml) and allowed to cool to ambient temperature, extracted with ether, washed successively with dilute hydrochloric acid, water, potassium hydrogen carbonate solution, dried, concentrated and applied to thin layer of silica gel. The major product (200 mg) was crystallized from methanol, m.p. 108–112°C, $[\alpha]_D^{20}$ +120° (*c* 1·2). IR-spectrum 1 719, 1 275 cm^{-1}. wircular dichroism: Δε −0·87 (250 nm), 0 (238 nm), +3·20 (230 nm). For $C_{34}H_{50}O_3$ (506·7) calculated: 80·58% C, 9·95% H; found: 80·31% C, 9·90% H.

1α-Methanesulfonyloxy-3β,5-epoxy-4α-methyl-A-homo-B,19-dinor-5β-,10α-cholestane (*XVII*)

The hydroxy derivative *XV* (170 mg) was treated with methanesulfonyl chloride (0·15 ml) in pyridine (1·5 ml) at 0°C for 20 h. The mixture was worked up and the product crystallized from heptane, m.p. 116–117°C (135 mg), $[\alpha]_D^{20}$ +49° (*c* 0·7). For $C_{28}H_{48}O_4S$ (480·7) calculated: 69·95% C, 10·06% H; found: 70·14% C, 10·18% H.

3β,5-Epoxy-4aα-methyl-A-homo-B,19-dinor-5β,10α-cholestane (*XVIII*)

The methanesulfonate *XVII* (15 mg) was heated at reflux temperature with a solution of lithium aluminum hydride (c. 100 mg) in tetrahydrofuran (5 ml) for 5 h. The excess reagent was decomposed with several drops of sodium sulfate solution, the mixture poured on a column of sodium sulfate and the product eluted with ether. The eluate was concentrated and separated into two components by thin layer chromatography. The polar component (7 mg) was identical with the unsaturated compound *V*, the non-polar component (7 mg) crystallized from methanol, m.p, 71–72°C, the IR spectrum and mixture m.p. prove identity with a sample obtained by catalytic hydrogenation of the compound *V* according to ref.[1].

3β,5-Epoxy-4aα-methyl-A-homo-B,19-dinor-5β,10α-cholestan-1-one (*XIX*)

A solution of the hydroxy derivative *XV* (30 mg) in pyridine (0·5 ml) was added to a stirred suspension of chromium trixoide (100 mg) in pyridine (1 ml) at 0°C. After 20 h the mixture was poured in potassium hydrogen carbonate, the product extracted with ether and washed with dilute hydrochloric acid and water. After drying the product was purified by thin layer chromatography on silica gel (benzene). The oily product solidified after some time to give an amorphous mass, m.p. 49–51°C, $[\alpha]_D^{20}$ +86° (*c* 1·3). IR spectrum: 1 709 cm^{-1}. Circular dichroism: $\Delta\varepsilon_{300}^{CH_3OH}$ +0·29. For $C_{27}H_{44}O_2$ (400·6) calculated: 80·94% C, 11·07% H; found: 80·64% C, 10·96% H.

2-Benzylidene-3β,5-epoxy-4aα-methyl-A-homo-B,19-dinor-5β,10α-cholestan-1-one (*XX*)

Ethanolic sodium ethoxide (4%, 1 ml) was added to a solution of the ketone *XIX* (50 mg) and benzaldehyde (0·3 ml) in ethanol (2 ml). After 20 h the mixture was diluted with a saturated aqueous solution of sodium chloride, the product taken up in ether, washed with water and dried. After thin-layer chromatography on silica gel (benzene), the main component (R_F 0·75) was crystallized from methanol, m.p. 148–149°C (40 mg), $[\alpha]_D^{20}$ +311° (*c* 0·9) IR spectrum: 1 691, 1 618, 1 577, 1 509, 1 496, 1 190, 1 074, 1 015, 698 cm^{-1}. For $C_{34}H_{48}O_2$ (488·7) calculated: 83·55% C, 9·90% H; found: 84·41% C, 9·76% H.

3β,5-Epoxy-4aα-methyl-A-homo-B,19-dinor-5β,10α-cholestan-1β-ol (*XXI*)

The ketone *XIX* (290 mg) was reduced with lithium tri-tert-butoxyaluminum hydride (700 mg) in tetrahydrofuran (3 ml). After 20 h the mixture was decomposed with dilute hydrochloric acid, the product extracted with ether, washed with water and the solvent removed *in vacuo*. The residue was purified by thin layer chromatography on silica gel. The major product (*XXI*, 220 mg) melts at 62–65°C, $[\alpha]_D^{20}$ +7° (*c* 1·0); IR spectrum ($5 \cdot 10^{-5}$ mol l^{-1}): 3 556, 1 002 cm^{-1}. For $C_{27}H_{46}O_2$ (402·6) calculated 80·54% C, 11·52% H; found: 80·68% C, 11·58% H. The minor product was found to be identical with the epimeric hydroxy derivative *XV*.

1β-Benzoyloxy-3β,5-epoxy-4aα-methyl-A-homo-B,19-dinor-5β,10α-cholestane (*XXII*)

The hydroxy derivative *XXI* (150 mg) was benzoylated by treatment with benzoyl chloride (0·1 ml) in pyridine (0·1 ml) at room temperature for 20 h. The mixture was worked up in usual manner and the product was purified by thin layer chromatography. The benzoate *XXII* (101 mg) melts at 110—111°C (acetone, methanol), $[\alpha]_D^{20}$ −57° (*c* 1·1). Circular dichroism (heptane): Δε −1·85 (243 nm), 0 (233 nm), +2·26 (222 nm). For $C_{34}H_{50}O_3$ (506·7) calculated: 80·58% C, 9·95% H; found: 80·51% C, 9·90% H.

4aα-Methyl-A-homo-B,19-dinor-5β,10α-cholestan-3β-ol (*XXIII*)

A solution of *XVIII* (36 mg) in acetic acid (2 ml) was shaken with platinum catalyst (200 mg) under hydrogen atmosphere for 12 h. The catalyst was filtered off, the solution concentrated under reduced pressure and the residue applied to a thin layer of silica gel. The major component (30 mg) was identical with the starting compound *XVIII*, the minor product (4 mg) was identical with the minor product of hydrogenation of the unsaturated epoxy derivative *V*, *i.e.* with the alcohol *XXIII*. The m.p. 133—135°C was undepressed on admixture with the sample prepared earlier[1], IR spectrum: 3 625, 1 040 cm^{-1}.

3β-Benzoyloxy-4aα-methyl-A-homo-B,19-dinor-5β,10α-cholestane (*XXIV*)

The alcohol *XXIII* (31 mg) was benzoylated with benzoyl chloride (0·1 ml) in pyridine (0·1 ml). After 4 h the mixture was worked up and the product purified by thin layer chromatography (30% ether in light petroleum), $[\alpha]_D^{20}$ +1° (*c* 1·2); IR spectrum: 1 718, 1 275 cm^{-1}. For $C_{34}H_{52}O_2$ (492·8) calculated: 82·87% C, 10·63% H; found: 83·01% C, 10·70% H.

4aα-Methyl-A-homo-B,19-dinor-5β,10α-cholestan-3-one (*XXV*)

a) The alcohol *XXIII* (170 mg) was oxidized at 20°C following the Jones procedure. After 5 min the mixture was poured into saturated aqueous potassium hydrogen carbonate solution (200 ml), the product taken up in ether, washed with water, dried with sodium sulfate and after evaporation purified by thin layer chromatography. M.p. 93—94°C (acetone). IR spectrum: 1 705 cm^{-1}. For $C_{27}H_{46}O$ (386·6) calculated: 83·87% C, 11·99% H; found: 83·69% C, 12·06% H.

b) The alcohol *XXVI* (15 mg) was oxidized analogously with Jones reagent and the product was found identical with that prepared under *a*.

4aα-Methyl-A-homo-B,10α-cholestan-3α-ol (*XXVI*)

The ketone *XXV* (140 mg) was added to a boiling solution of lithium aluminum hydride (c. 250 mg) in dioxane (5 ml). After 25 min the mixture was worked up in conventional manner and the mixture separated by thin layer chromatography to give two components. The non-polar component (70 mg) proved identical with the 3β-hydroxy derivative *XXIII*, the polar component (63 mg, *XXVI*) melts at 104—106°C (methanol), $[\alpha]_D^{20}$ −30° (*c* 0·9). IR spectrum: 3 625, 1 057, 1 021 cm^{-1}. For $C_{27}H_{48}O$ (388·6) calculated: 83·43% C, 12·45% H; found: 83·25% C, 12·41% H. Reduction with bulky lithium tri-tert-butoxyaluminum hydride yielded the isomers (*XXVI* and *XXIII*) in the same proportion.

3α-Benzoyloxy-4aα-methyl-A-homo-B,19-dinor-5β,10α-cholestan (*XXVII*)

The hydroxy derivative *XXVI* (35 mg) was benzoylated in similar manner as the compound *XXIII*, the product crystallized from ether–methanol mixture, m.p. 93—94°C, $[\alpha]_D^{20}$ −14° (*c* 0·6). IR

spectrum: 1 719, 1 278 cm^{-1}. For $C_{34}H_{52}O_2$ (492·8) calculated: 82·78% C, 10·64% H; found: 82·95% C, 10·46% H.

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