OXIDATION AND EPOXIDATION OF 4,4-DIMETHYL-A-HOMO-5-CHOLESTEN-4a-OLS*

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Oxidation of four stereoisomeric 3-acetoxy-4,4-dimethyl-A-homo-5-cholesten-4a-ols *I*—*IV* with Sarett's and Jones's reagent was investigated. 4aβ-Hydroxy derivatives *II* and *IV* afforded corresponding enones *V* and *XVI* as the main products, while in the case of 4aα-hydroxy derivatives *I* and *III* the formation of 5β,6β-epoxides was observed both in the oxidation according to Jones and in the oxidation with the Sarett's reagent. The study of the stereochemistry of epoxidation of olefins *I*—*IV* and their derivatives showed that the epoxidation of the 5,6-double bond takes place preferentially from the β-side of the cyclic system. On the basis of ^{1}H NMR data the preferred conformation of the seven-membered ring A in the allylic alcohols *I*—*IV* was determined; on its basis the effects leading to different behaviour of epimers *I*, *III* and *II*, *IV* during oxidation are discussed.

The formation of epoxides was observed not only during the oxidation of steroidal and terpenic allylic alcohols with acid Cr(VI) reagents (chromium trioxide in acetic acid, Jones's reagent)[1–4], but also when they were oxidized with Collins[5–8], Corey's[6,7] and Sarett's[9] reagent. It is known[1,2] that allylic alcohols in which the oxidation rate of the hydroxyl group is decreased in consequence of the cisoid nature of the expected enone and/or the non-application of the stereoelectronic factor show an increased tendency to the formation of epoxides during the oxidation with Cr(VI) reagents. In connection with our stereochemical studies of 4,4-dimethyl-A-homocholestane derivatives[10–13] the question arose of how the oxidation of 4a-hydroxy-5,6-unsaturated derivatives of this series would proceed, where, in view of the cisoid nature of the expected enone and the flexibility of the seven-membered ring A, the oxidation rate of one of the epimers could be decreased to such an extent that the formation of the products of epoxidation of the 5,6-double could take place. In this study we describe the oxidation of all four stereoisomeric 3-acetoxy-4,4-dimethyl-A-homo-5-cholesten-4a-ols *I*—*IV* described earlier[13], both with Sarett's and the Jones's reagent, further the stereochemistry of the epoxidation of olefins *I*—*IV* and their derivatives, and the determination of the preferred conformation of the seven-membered ring A of allylic alcohols *I*—*IV* by means of ^{1}H NMR spectroscopy.

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Irrelevant of the configuration of the 3-acetoxy group the oxidation of 4aβ-hydroxy--5,6-unsaturated derivatives *II* and *IV* with Sarett's and Jones's reagent afforded the expected enones *V* and *XVI* as the main products (Table I). In agreement with the proposed structure their ^{1}H NMR spectra contain a distinct signal of only one olefinic proton, appearing as a multiplet at $\delta = 5{\cdot}25$ ppm. However, from the IR data it followed that the A-ring of derivatives *V* and *XVI* is preferentially in the conformation in which the 4a-carbonyl group and the 5,6-double bond are not coplanar ($\nu_{(CO)} = 1\,701$ cm^{-1} for *V* and 1 691 cm^{-1} for *XVI*, $\nu_{(C=C)} = 1\,658$ cm^{-1} for *V* and 1 660 cm^{-1} for *XVI*). The epimeric 4aα-hydroxy derivatives *I* and *III* afforded on oxidation with Sarett's reagent the products of epoxidation of the 5,6-double bond in addition to the expected enones *V* and *XVI*, *i.e.* the epoxy alcohols *VI* and *XVII* and keto epoxides *VII* and *XVIII*. Oxidation of 4aα-hydroxy derivatives *I* and *III* with Jones's reagent afforded keto epoxides *VII* and *XVIII* only (Table I).

For correlation of the structures of epoxides *VI*, *VII*, *XVII* and *XVIII*, formed during the oxidation of allylic alcohols *I* and *III* with Cr^{VI} reagents, the stereochemistry of the epoxidation of olefins *I*–*IV* and some of their derivatives was also investigated. Epoxidations were carried out with *m*-chloroperbenzoic acid in chloroform at room temperature. In the case of epoxidation of olefins *I*–*IV* and that of 3,4a-diacetoxy derivatives *XXIII*–*XXVI* and 3β,4aα-diol *XXVII*, described

TABLE I

Percentual representation of the products of oxidation and epoxidation of allylic alcohols *I*–*IV*

Compound	Reagent	Δ^5-4a-one	5β,6β-epoxy-4a-ol	5β,6β-epoxy-4a-one
I	Sarett	53 (*V*)	11 (*VI*)	35 (*VII*)
	Jones	—	—	73 (*VII*)
	MCPBA[a]	—	81 (*VI*)[b]	—
II	Sarett	87 (*V*)	—	—
	Jones	96 (*V*)	—	—
	MCPBA[a]	—	90 (*XIII*)	—
III	Sarett	35 (*XVI*)	42 (*XVII*)	21 (*XVIII*)
	Jones	—	—	80 (*XVIII*)
	MCPBA[a]	—	87 (*XVII*)	—
IV	Sarett	86 (*XVI*)	—	—
	Jones	77 (*XVI*)	—	—
	MCPBA[a]	—	80 (*XX*)	—

[a] *m*-Chloroperoxybenzoic acid; [b] the structure of the by-product of the allylic rearrangement (14%) will be published later.

earlier[13], as well as in the epoxidation of enones *V* and *XVI*, only one of the two possible epimeric epoxides (see Tables I and II) could be isolated from the reaction mixture. The structures of the epoxides *VI*, *VII*, *XI–XIV* and *XVII–XXI* obtained were determined by means of chemical correlations and ^{1}H NMR data. Acetylation of 4a-hydroxy epoxides *VI*, *XIII*, *XVII* and *XX* and 3β,4aα-dihydroxy epoxide *XII* showed that during the epoxidation of 3,4a-diacetoxy derivatives *XXIII–XXVI* and 3β,4aα-dihydroxy derivative *XXVII* epoxides of the same configuration of the 5,6-epoxide ring are formed as in the epoxidation of corresponding 3-acetoxy-4a-hydroxy derivatives *I–IV*. Oxidation of 3β- and 3α-acetoxy-4a-hydroxy epoxides *VI*, *XIII* and *XVII*, *XX* to corresponding 4a-keto epoxides *VII* and *XVIII* then demonstrated the same configuration of the 5,6-epoxide ring even in the products of epoxidation of enones *V* and *XVI*. A correlation between 3β- and 3α-substituted 5,6-epoxides was carried out by oxidation of 3β-hydroxy ketone *VIII* and 3α,4a-diols *XV* and *XXII*, obtained by elimination of the 3-acetoxy group from derivatives *VII*, *XIII* and *XX*, to the same diketone *IX*. In the oxidation of diols *XV* and *XXII* 4aβ-hydroxy ketone *X* was a by-product in the ^{1}H NMR spectrum of which the signal of one epoxide proton at $\delta = 3{\cdot}03$ ppm is apparent which – in agreement with the proposed structure – appears as a doublet ($J = 2$ Hz) and the signal of one proton on the carbon atom carrying the hydroxy group, appearing as a singlet at $\delta = 2{\cdot}93$ ppm. 4aβ-hydroxy ketone *X* was oxidized with Sarett's reagent to diketone *IX*. Hence the above mentioned chemical correlations demonstrate that the configuration of the 5,6-epoxide ring in the substances investigated, *i.e.* *VI*, *VII*, *XI–XIV* and *XVII* to *XXI*, is the same in all instances. In the ^{1}H NMR spectra of 4a-hydroxy epoxides *VI*, *XIII*, *XVII* and *XX* the signal may be observed of only one epoxide proton, appearing as a doublet at $\delta = 2{\cdot}87-3{\cdot}41$ ppm with the coupling constant $J = 2{\cdot}0-2{\cdot}8$ Hz. On the basis of the data published in literature[14] it may thus be assumed that the 5,6-epoxide ring of epoxides *VI*, *XIII*, *XVII* and *XX* has configuration β, and in view of the above mentioned chemical correlations the other epoxides investigated, *VII*, *XI*, *XII*, *XIV*, *XVII–XIX* and *XXI*, may also be considered as

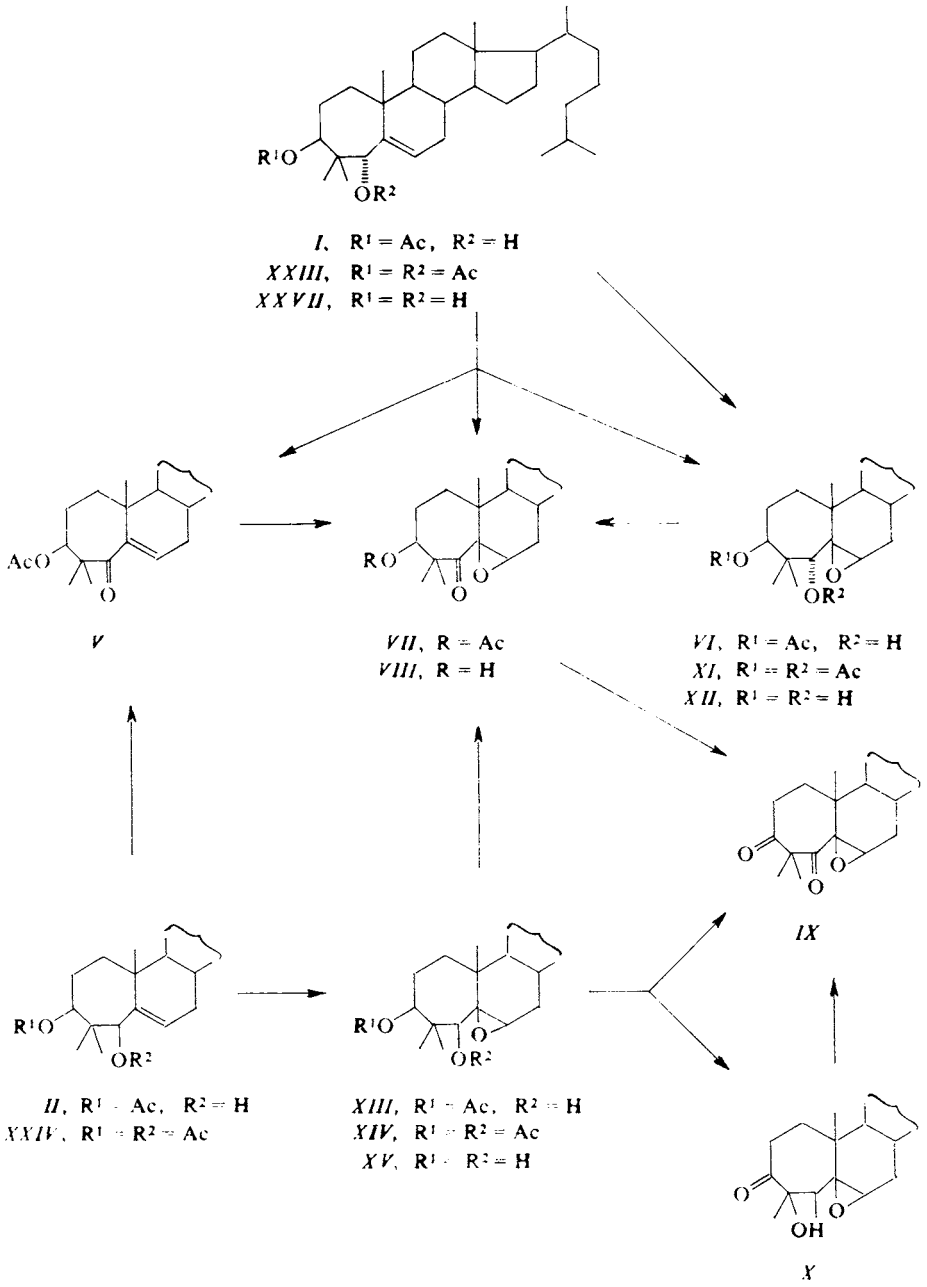
TABLE II

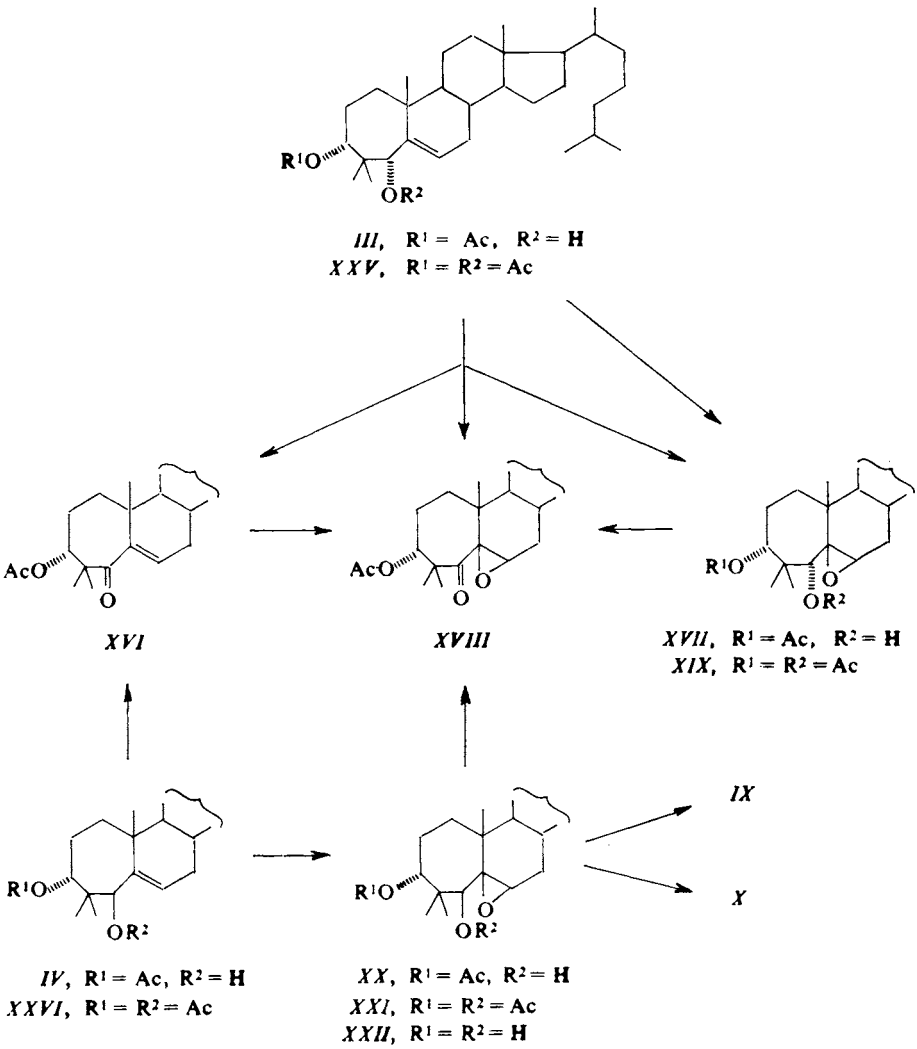
Yields (in % of the overall yield) of 5β,6β-epoxides in the epoxidation of 3,4a-disubstituted Δ^5-olefins

Olefin	*V*	*XVI*	*XXIII*	*XXIV*	*XXV*	*XXVI*	*XXVII*
5β,5β-Epoxide	*VII*[a]	*XVIII*	*XI*	*XIV*	*XIX*	*XXI*	*XII*[b]
Yield	64	88	87	87	80	82	83

[a] 25% of the starting olefin *V*; [b] the structure of the by-product of the allylic rearrangement (10%) will be published later.

5β,6β-epoxides. Epoxidation of the 5,6-double bond of the 4,4-dimethyl-A-homo--5-cholestene derivatives studied proceeds preferentially from the β-side of the cyclic





system, 5β,6β-epoxides being also the products of the competing epoxidation reaction in the oxidation of 4aα-hydroxy-5,6-unsaturated derivatives *I* and *III*.

In order to explain the preferential formation of 5β,6β-epoxides both in the epoxidation of the investigated 3,4a-disubstituted 4,4-dimethyl-A-homo-5-cholestene derivatives and in the oxidation of 4aα-hydroxy-5,6-unsaturated derivatives *I* and *III* with Sarett's and Jones's reagent, it was necessary to determine the preferred conformation of the seven-membered ring A of the starting olefins *I*–*IV*, for which the ^{1}H NMR data were made use of. Since the signal of the $C_{(3)}$—H proton in derivatives *I* and *II* forms a complex multiplet, the conformation of the ring A of derivatives

III and *IV* will be discussed first, where the signal of this proton forms a well-resolved doublet of doublets, with $J_{3\beta,2\alpha} = 9{\cdot}6$ Hz and $J_{3\beta,2\beta} = 4{\cdot}0$ Hz for compound *III* and $J_{3\beta,2\alpha} = 9{\cdot}8$ Hz and $J_{3\beta,2\beta} = 4{\cdot}7$ Hz for compound *IV*. The vicinal coupling constants $J_{3,2}$ permit the determination of the dihedral angles of corresponding hydrogen atoms $\theta_{H,H}$ by means of the known Karplus relation[15], ${}^3J_{H,H} = f(\theta)$. However, the vicinal coupling constants in the fragment H—C—C—H depend[15] not only on the angle θ, but also on the electronegativity of the substituents, bond lengths and the valence angles $\theta = \sphericalangle HCC$, $\theta = \sphericalangle CCH$, and therefore it is indispensable to adjust the relation ${}^3J_{H,H}$ directly for a given structural system or a system structurally as close to this as possible. Since an adjustement for the cycloheptane ring has not been carried out so far, we used the relation

$$ {}^3J_{H,H} = 5{\cdot}95 - 1{\cdot}35 \cos\theta + 5{\cdot}45 \cos 2\theta - 0{\cdot}45 \cos 3\theta \qquad (1) $$

adjusted for the closest cyclic homologue cyclohexane and used for conformational analysis of 1,6-anhydro-β-D-hexopyranoses[16]. The effect of the electronegativity of the acetoxy group on $J_{3,2}$ was respected in the usual manner[17] by using the relation

$$ J_{corr} = J_{exp} \cdot (1 - 0{\cdot}1\,\Delta E)^{-1}, \qquad (2) $$

where ΔE is the difference in the electronegativities[18] of the acetoxy group ($E = 3{\cdot}8$) and the hydrogen ($E = 2{\cdot}1$), J_{corr} is the value of the vicinal coupling constant calculated from the equation (*1*) and J_{exp} is the experimentally determined coupling constant value. Using the equations (*1*) and (*2*) the dihedral angles $\theta_{3\beta,2\alpha}$ and $\theta_{3\beta,2\beta}$ were calculated, which are presented in Table III together with the experimental vicinal coupling constants. Several conformations of the seven-membered ring A are in agreement with the calculated dihedral angles which are approximately equal for both allylic alcohols *III* and *IV* investigated (about 160° and 45°), *i.e.* $TC_{(10)}$, $TC_{(2)}$, $C_{(3)}$, $B_{(2)}$, $B_{(10)}$, $TB_{(4)}$, $TB_{(3)}$, $TB_{(4a)}$, $TB_{(5)}$. Since the calculations of the conformational energies have shown[19–23] that the lowest energy of the cycloheptane ring corresponds to a twist-chair conformation, the conformations $TC_{(10)}$ and $TC_{(2)}$ of the ring A may be considered as the most probable. However, the steric strain in the conformation $TC_{(2)}$ is higher than in the conformation $TC_{(10)}$, and moreover in conformation $TC_{(2)}$ strong steric interaciton between the 4α-methyl group and the 1α-hydrogen atom would take place. Therefore we consider that from the point of view of the NMR time scale the conformation $TC_{(10)}$ (Fig. 1) is the preffered conformation of the seven-membered ring A of the allylic alcohols *III* and *IV*, where the angular 19-methyl group and the carbon atom at $C_{(9)}$ are in the isoclinal position and the 3α-acetoxy group is approximately equatorial. The 4a-hydroxy group in derivative *III* is aproximately equatorial, while in derivative *IV* it is approximately axial.

The signal of the proton on $C_{(3)}$ in derivative *II* forms a broad doublet. On the basis of decoupling experiments its coupling ($^4J \leqq 1$ Hz) with the 4aα-proton was determined. Approximate values of the coupling constants $J_{3,2}$ (Table III) were determined from the spectrum measured on irradiation of the 4aα-proton signal. In derivative *I* the extraction of $J_{3,2}$ values from the spectrum measured in deuteriochloroform is practically impossible since the 3α-proton forms a complex multiplet, probably in consequence of virtual and long-range couplings. The spectrum of derivative *I* in deuteriobenzene showed, however, a broad doublet for the 3α-proton, and similarly as in derivative *II* its coupling ($^4J \leqq 1$ Hz) with the 4aβ-proton was found and the constants $J_{3,2}$ determined (Table III). Even though the accuracy of the determination of these constants in derivatives *I* and *II* is low (±0·5 Hz), they were used for the calculation of approximate dihedral angles $\theta_{3\alpha,2\alpha}$ and $\theta_{3\alpha},\theta_{2\beta}$ (Table III), using equations (*1*) and (*2*). The calculated dihedral angles are approxi-

TABLE III
Calculated dihedral angles $\Phi_{3,2}$ of allylic alcohols *I*—*IV*

Compound	Observed			Calculated $\Phi_{H,H}$ [O]	
	δ_{3H}, ppm	$J_{3,2\alpha}$, Hz	$J_{3,2\beta}$, Hz	$\Phi_{3,2\alpha}$	$\Phi_{3,2\beta}$
I[a]	4·61	4·6	1·2	44	72
II	4·78	4·5	1·3	44	71
III	4·48	9·6	4·0	160	48
IV	4·95	9·8	4·7	161	43

[a] In deuteriobenzene.

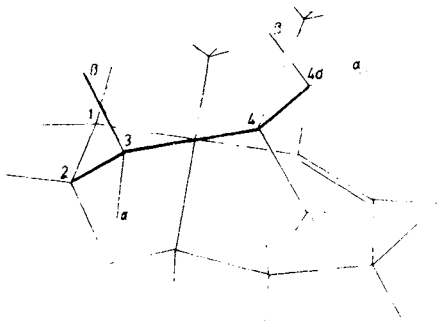


FIG. 1
Conformation $TC_{(10)}$ of the A ring of allylic alcohols *I*—*IV*

mately the same for both allylic alcohols *I* and *II* studied (about 44° and 70°), and they satisfy the same $TC_{(10)}$ conformation of the seven-membered ring A as in derivatives *III* and *IV* (Fig. 1). Further conformations of the seven-membered ring A, conforming to the calculated dihedral angles, *i.e.* the conformations $C_{(3)}$, $TC_{(2)}$, $B_{(2)}$, $B_{(10)}$, $TB_{(3)}$, $TB_{(4)}$, $TB_{(4a)}$ $TB_{(5)}$, were eliminated on the basis of the same considerations as used above. Hence, it may be assumed that the change of the configuration of the 3-acetoxy group does not lead to a substantial change in the conformation of the seven-membered ring A from the point of view of the NMR time scale, and the 3β-acetoxy group in derivatives *I* and *II* assumes an approximately axial position, while the 4a-hydroxy group is approximately equatorial in derivative *I* and approximately axial in derivative *II*. The calculation of dihedral angles $\theta_{3,2}$ by the method of Slessor and Tracey[24], applied to the fragment $C_{(2)}H_2—\overset{H}{\underset{|}{C}}_{(3)}OCOCH_3$, leads also to the same conclusion on the preffered conformation of the ring A of the derivatives *I*–*IV*, because the values of the dihedral angles calculated by this method differ from the values given in Table III by less than 8°. Thus from the point of view of the NMR time scale the conformation $TC_{(10)}$ may be considered as the preferred conformation of the seven-membered ring A in equilibrium mixtures of the conformers of allylic alcohols *I*–*IV*.

Conformation $TC_{(10)}$ permits a satisfactory explanation of both the stereochemistry of epoxidation of derivatives *I*–*IV*, *XXIII*–*XXVII* and the difference in behaviour of epimeric allylic alcohols *I*, *III* and *II*, *IV* in the oxidation with Sarett's and Jones's reagent. In the $TC_{(10)}$ conformation the 4α-methyl group displays a strong steric hindrance to the access of the reagent to the 5,6-double bond from the α-side of the cyclic system. The 4aβ-hydroxy group makes with the 5,6-double bond in this conformation $TC_{(10)}$ an angle of about 145°, whereas for the 4aα-hydroxy group this angle is about 35°, both the 4aα- and the 4aβ-hydroxy group being oriented above the plane of the 5,6-double bond, *i.e.* to the β-side of the cyclic system. In the case of 4aβ- and 4aα-hydroxy derivatives *I*–*IV* the formation of 5β,6β-epoxides is evidently ruled by the directing effect of the allylic hydroxy group[25–28], which, probably, is also the directing effect in the epoxidation of 3β,4aα--diol *XXVII*. Under the assumption that the acetylation of the 4a-hydroxy group does not lead to a change in the preferred conformation of the seven-membered ring A, the preferential formation of 5β,6β-epoxides in the epoxidation of diacetoxy derivatives *XXIII*–*XXVI* would be given by the steric hindrance to the access of the reagent from the α-side of the cyclic system, displayed by the 4aα-methyl group in the conformation $TC_{(10)}$.

The difference in the behaviour of epimeric allylic alcohols *I*, *III* and *II*, *IV* in the oxidation with Sarett's and Jones's reagent cannot be explained by the stereoelectronic factor[1], because the angle between the 4a-hydroxy group and the 5,6-double bond

in conformation $TC_{(10)}$ is about 35°C for 4aα-epimer and about 145°C for 4aβ-epimer. It is known[1], that the rate of oxidation of secondary saturated and allylic alcohols is also affected by steric strain, *i.e.* that the more strained alcohol is oxidized more rapidly. Recently the role of the accessibility of the α-proton to the attack of base[4,7] in oxidation was also stressed. In conformation $TC_{(10)}$ the 4aβ-hydroxy group of derivatives *II* and *IV* is exposed to strong steric interactions with the 19-methyl group and the 1β-hydrogen atom, while the 4aα-hydrogen atom is relatively easily accessible to the attack of the base. The decrease of the steric strain in the transition state during the passage to enone *V*, or *XVI* resp., and the easy steric accessibility of the 4aα-proton evidently cause the intramolecular transfer of oxygen from the chromate ester to the 5,6-double bond not to take place even though this oxygen transfer would lead to the transition state on the β-side of the cyclic system, which is sterically favourable for epoxidation. In contrast to this, in the case of epimeric 4aα-hydroxy derivatives *I* and *III* the 4aα-hydroxy group is exposed to lesser steric interactions in conformation $TC_{(10)}$, so that the decrease of steric strain in the transition state during the transition to enone *V*, or *XVI* resp., will not be as distinct as in the case of 4aβ-hydroxy derivatives *II*, *IV*. Moreover, the attack of the base to the 4aβ-proton is substantially decreased owing to the strong steric hindrance displayed by the 19-methyl group and the 1β-hydrogen atom. In consequence of these factors the oxidation rate of the 4aα-hydroxy group is evidently decreased to such an extent that an alternative intramolecular oxygen transfer from the chromate ester takes place, which in view of the orientation of the 4aα-substituent in conformation $TC_{(10)}$ above the 5,6-double bond plane (*i.e.* to the β-side of the cyclic system) proceeds by the known cyclic mechanism under formation of 5β,6β-epoxides.

These results, in addition to the studies of Swiss authors[9], represent a further example of the formation of epoxides during the oxidation of steroid allylic alcohols with Sarett's reagent.

EXPERIMENTAL

The melting points were determined on a Kofler block and they are not corrected. Optical rotations were measured in chloroform. The infrared spectra were measured on a Zeiss UR 20 instrument in tetrachloromethane, unless stated otherwise. The ^{1}H NMR spectra were measured on a Varian XL-200 (200 MHz) instrument or on spectrometers Tesla B 476 (60 MHz) and Varian HA 100 (100 MHz) in deuteriochloroform with tetramethylsilane as internal reference, at 22°C. Chemical shifts are given in δ-scale. The spectra were interpreted only as first order spectra. The identity of the samples prepared in different ways was checked by mixture melting points and infrared spectra. The term "conventional work-up" means: The solution was washed with 5% hydrochloric acid, 5% potassium hydrogen carbonate solution in water, dried over sodium sulfate and the solvent evaporated in a vacuum. Preparative chromatography of crude products was carried out on silica gel plates (20 × 20 × 0·07 cm) in light petroleum–ether (8 : 2), unless stated otherwise. Corresponding zones were combined, extracted with ether and the solvent evaporated under reduced pressure.

3β-Acetoxy-4,4-dimethyl-A-homo-5-cholesten-4a-one (*V*)

a) Chromium trioxide (120 mg) was added to a solution of 4,4-dimethyl-A-homo-5-cholestene-3β,4aα-diol 3-acetate (*I*), ref.[13] (120 mg), in pyridine (6 ml) and the mixture was allowed to stand at room temperature for 2 days. The conventional work-up gave 120 mg of a crude product which was submitted to preparative chromatography on 3 silica gel plates. The corresponding least polar zones afforded 63·5 mg of ketone *V* which was crystallized from methanol (50 mg), m.p. 86–88°C, $[\alpha]_D^{20} = +69°$ (*c* 0·5). Infrared spectrum: 1 743, 1 660, 1 702 cm^{-1}. ^1H NMR spectrum (100 MHz): 0·69 (s, 18-CH_3); 0·87 (d, 26 + 27-CH_3, $J = 6·0$ Hz); 0·91 (d, 21-CH_3, $J = 6·0$ Hz); 0,96, 1·03, 1·15 (s, 19-CH_3; s, 4,4-dimethyl); 2·04 (s, acetate); 5·25–5·30 (mt, 3α + 6-H). For $C_{32}H_{52}O_3$ (484·7) calculated: 79·28% C, 10·81% H; found: 79·06%, 10·66% H.

b) Chromium trioxide (150 mg) was added to a solution of 4,4-dimethyl-A-homo-5-cholestene-3β,4aβ-diol 3-acetate (*II*), ref.[13] (150 mg), in pyridine (6 ml) and the mixture was allowed to stand at room temperature overnight. The conventional work-up afforded 150 mg of product, which was chromatographed on 3 preparative silica gel plates. Corresponding combined zones were worked up to give 130 mg of ketone *V* which was crystallized from methanol (103 mg), m.p. 86–88°C, $[\alpha]_D^{20} = +69°$ (*c* 0·5).

c) Jones's reagent (0·5 ml) was added to a solution of alcohol *II*, ref.[13] (50 mg), in acetone (3 ml) and the mixture was allowed to stand at room temperature for 5 min under occasional shaking. It was then poured into water and extracted with ether. The extract was washed with a 5% potassium hydrogen carbonate solution and water, then dried over sodium sulfate and the solvent evaporated in a vacuum. The residue (50 mg) was chromatographed on preparative silica gel plate to give 48 mg of ketone *V* which was crystallized from methanol (26 mg), m.p. 86–88°C, $[\alpha]_D^{20} = +69°$ (*c* 0·5).

4,4-Dimethyl-5,6β-epoxy-A-homo-5β-cholestane-3β,4aα-diol 3-Acetate (*VI*)

a) Working up of the combined less polar zones after the isolation of ketone *V* in the preceding experiment (under *a*) afforded 13·7 mg of epoxide *VI* which was crystallized from methanol, m.p. 127–129°C, $[\alpha]_D^{20} = +31°$ (*c* 0·5). Infrared spectrum: 1 740, 1 246, 3 510 cm^{-1}. ^1H NMR spectrum (200 MHz): 0·65 (s, 18-CH_3); 0·86, 0·87 (d, 26-CH_3; d, 27-CH_3, $J = 6·6$ Hz); 0·87, 0·92, 1·07 (s, 19-CH_3; s, 4,4-dimethyl); 2·09 (s, acetate); 3·36 (d, 6α-H, $J_{6\alpha,7\beta} = 2·1$ Hz); 4·02 (s, 4aβ-H); 4·74 (t, 3α-H, $J_{3\alpha,2\alpha} = J_{3\alpha,2\beta} = 3·8$ Hz). For $C_{32}H_{54}O_4$ (502·75) calculated: 76·44% C, 10·83% H; found: 76·56% C, 11·05% H.

b) *m*-Chloroperbenzoic acid (180 mg) was added to a solution of olefin *I*, ref.[13] (180 mg), in chloroform (10 ml) and the mixture was allowed to stand at room temperature for 30 min. After pouring into water the product was extracted with ether, the extract was washed with a saturated aqueous potassium carbonate solution and water, dried over sodium sulfate and the solvent evaporated in a vacuum. The residue (178 mg) was chromatographed on 3 preparative silica gel plates to give 160 mg of epoxide *VI* which was crystallized from methanol (120 mg), m.p. 127–129°C, $[\alpha]_D^{20} = +31°$ (*c* 0·5).

3β-Acetoxy-4,4-dimethyl-5,6β-epoxy-A-homo-5β-cholestan-4a-one (*VII*)

a) Working up of the most polar combined zones after separation of ketone *V* and epoxide *VI* in the preceding experiments (under *a*) afforded 43·5 mg of keto epoxide *VII* which was crystallized from methanol (26 mg), m.p. 137–139°C, $[\alpha]_D^{20} = -61°$ (*c* 0·5). Infrared spectrum (chloroform): 1 732, 1 258, 1 248, 1 037, 1 028, 1 714, 959 cm^{-1}. ^1H NMR spectrum (200 MHz): 0·64 (s, 18-CH_3); 0·87 (d, 26 + 27-CH_3, $J = 6·5$ Hz); 0·91 (d, 21-CH_3, $J = 6·5$ Hz); 0·97, 1·02,

1·19 (s, 19-CH_3; s, 4,4-dimethyl); 2·08 (s, acetate); 3·31 (bd, 6α-H, $J_{6\alpha,7\beta}$ = 1·4 Hz); 5·53 (dd, 3α-H, $J_{3,2}$ = 6 + 11·2 Hz). CD spectrum (dioxane): $\Delta\varepsilon_{300} = -2{\cdot}99$. For $C_{32}H_{52}O_4$ (500·7) calculated: 76·75% C, 10·47% H; found: 76·42% C, 10·57% H.

b) Chromium trioxide (30 mg) was added to a solution of alcohol *VI* (30 mg) in pyridine (3 ml) and the mixture was allowed to stand at room temperature overnight. The conventional work-up afforded 29 mg of product which was chromatographed on a preparative thin-layer plate of silicagel. The required zone gave after working up 25 mg of keto epoxide *VII* which was crystallized from methanol (15 mg), m.p. 137–139°C, $[\alpha]_D^{20} = -60°$ (*c* 0·5).

c) *m*-Chloroperoxybenzoic acid (140 mg) was added to a solution of olefin *V* (140 mg) in chloroform (8 ml) and the mixture allowed to stand at room temperature for 5 h. It was poured into water and extracted with ether, the extract washed with saturated aqueous solution of potassium carbonate and then water, dried over sodium sulfate and evaporated under reduced pressure. The residue (139 mg) was submitted to chromatography on 2 preparative thin-layer silica gel plates to give 116 mg of epoxide *VII* which was crystallized from methanol (90 mg), m.p. 137–139°C, $[\alpha]_D^{20} = -61°$ (*c* 0·5).

d) Chromium trioxide (60 mg) was added to a solution of alcohol *XIII* (60 mg) in pyridine (3 ml) and the mixture was allowed to stand at room temperature for 2 days. The conventional work-up gave 60 mg of a crude product which was separated by preparative thin-layer chromatography (1 plate) on silica gel to give 56 mg of ketone *VII* which was crystallized from methanol (43 mg), m.p. 137–139°C, $[\alpha]_D^{20} = -61°$ (*c* 0·5).

e) Jones's reagent (0·5 ml) was added to a solution of alcohol *I*, ref.[13], (50 mg) in acetone (3 ml) and the mixture was allowed to stand at room temperature under occasional shaking for 5 min. The mixture was poured into water and extracted with ether. The extract was washed with 5% aqueous solution of potassium hydrogen carbonate and water, dried over sodium sulfate and the solvent was evaporated in a vacuum. The residue (48 mg) was submitted to preparative chromatography on a silica gel plate to afford 37 mg of keto epoxide *VII* which was crystallized from methanol (25 mg), m.p. 137–139°C, $[\alpha]_D^{20} = -61°$ (*c* 0·5).

f) Alcohol *VIII* (50 mg) was acetylated with acetic anhydride (0·2 ml) in pyridine (3 ml) for 2 days. The conventional work-up afforded 49 mg of a product which was crystallized from methanol. Yield 27·5 mg of acetoxy derivative *VII*, m.p. 137–139°C, $[\alpha]_D^{20} = -61°$ (*c* 0·5).

4,4-Dimethyl-5,6β-epoxy-3β-hydroxy-A-homo-5β-cholestan-4a-one (*VIII*)

An aqueous solution of potassium hydrogen carbonate (80 mg, 1 ml) was added to a solution of acetoxy derivative *VII* (80 mg) in methanol (5 ml) and the mixture was refluxed for 1 h, poured into water and extracted with ether. The extract was washed with water, dried over sodium sulfate and the solvent evaporated under reduced pressure. The residue (75 mg) was crystallized from methanol to yield 50 mg of alcohol *VIII*, m.p. 238–240°C, $[\alpha]_D^{20} = -59°$ (*c* 0·5). Infrared spectrum (chloroform): 3 620, 1 042, 1 036, 1 709, 960 cm^{-1}. ^1H NMR spectrum (60 MHz): 0·63 (s, 18-CH_3); 0·86 (d, 26 + 27-CH_3, J = 6 Hz); 0·94, 1·10, 1·13 (s, 19-CH_3; s, 4,4-dimethyl); 3·27 (d, 6α-H, $J_{6\alpha,7\beta}$ = 2 Hz); 4·23 (mt, 3α-H). For $C_{30}H_{50}O_3$ (458·7) calculated: 78·55% C, 10·99% H; found: 78·14% C, 10·99% H.

4,4-Dimethyl-5,6β-epoxy-A-homo-5β-cholestane-3,4a-dione (*IX*)

a) Chromium trioxide (40 mg) was added to a solution of alcohol *VIII* (35 mg) in pyridine (3 ml) and the mixture was allowed to stand at room temperature overnight. The conventional

work-up gave 32 mg of a crude product which was chromatographed preparatively on a silica gel thin-layer plate in light petroleum–ether (9 : 1) to afford 28 mg of diketone *IX*. This was crystallized from methanol (15 mg), m.p. 150–152°C, $[\alpha]_D^{20} = -74°$ (*c* 0·5). Infrared spectrum: 1 730, 1 705, 964 cm^{-1}. For $C_{30}H_{48}O_3$ (456·7) calculated: 78·90% C, 10·59% H; found: 78·65% C, 10·43% H.

b) Chromium trioxide (50 mg) was added to a solution of diol *XV* (50 mg) in pyridine (4 ml) and the mixture was allowed to stand at room temperature overnight. The conventional work-up afforded 48 mg of a product which was separated chromatographically on a preparative thin-layer plate in light petroleum–ether (9 : 1). The corresponding less polar zone was worked up to give 26 mg of diketone *IX* which was crystallized from methanol (14 mg), m.p. 150–152°C, $[\alpha]_D^{20}$ −74° (*c* 0·5).

c) Chromium trioxide (80 mg) was added to a solution of diol *XXII* (80 mg) in pyridine (5 ml) and the mixture was allowed to stand at room temperature overnight. The conventional work-up gave 78 mg of a product which was purified by preparative thin-layer chromatography on a silica gel plate in light petroleum–ether (9 : 1). After working up the less polar zone 39 mg of diketone *IX* were obtained, which was crystallized from methanol (23 mg), m.p. 150–152°C, $[\alpha]_D^{20} =$ $= -73°$ (*c* 0·5).

d) Chromium trioxide (20 mg) was added to a solution of alcohol *X* (30 mg) in pyridine (3 ml) and the mixture was allowed to stand at room temperature overnight. The conventional work-up gave 29 mg of a product which was crystallized from methanol. Yield, 17 mg of diketone *IX*, m.p. 150–152°C, $[\alpha]_D^{20} = -74°$ (*c* 0·5).

4,4-Dimethyl-5,6β-epoxy-4aβ-hydroxy-A-homo-5β-cholestan-3-one (*X*)

a) Working up of the more polar zone after the separation of diketone *IX* in the preceding experiment (under *b*) afforded 14 mg of keto alcohol *X* which was crystallized from methanol (8 mg), m.p. 150–151°C, $[\alpha]_D^{20} = +13°$ (*c* 0·5). Infrared spectrum (chloroform): 3 620, 1 048, 1 705, 1 695, 984, 945, 912 cm^{-1}. ^1H NMR spectrum (60 MHz): 0·58 (s, 18-CH_3); 0·80 (d, 26 + 27-CH_3, $J = 6$ Hz); 1·07, 1·14, 1·19 (s, 19-CH_3; s, 4,4-dimethyl); 2·93 (s, 4aα-H); 3·03 (d, 6α-H, $J_{6\alpha,7\beta} = 2$ Hz). For $C_{30}H_{50}O_3$ (458·7) calculated: 78·55% C, 10·99% H; found: 78·32% C, 10·76% H.

b) Working up of the more polar zone after the separation of diketone *IX* in the preceding experiment (under *c*) afforded 28 mg of keto alcohol *X* which was crystallized from methanol (17 mg), m.p. 150–151°C. $[\alpha]_D^{20} = +13°$ (*c* 0·5).

4,4-Dimethyl-5,6β-epoxy-A-homo-5β-cholestane-3β,4aα-diol 3,4a-Diacetate (*XI*)

a) Alcohol *VI* (40 mg) was acetylated with acetic anhydride (0·1 ml) in pyridine (2 ml) at 30°C for 4 days. The conventional work-up afforded 40 mg of a product which was submitted to preparative thin-layer chromatography on one silica gel plate in light petroleum–ether (9 : 1), using a triple elution. Working up of combined corresponding zones afforded 30 mg of diacetoxy derivatives *XI* which was crystallized from methanol (19 mg), m.p. 129–131°C. Infrared spectrum (chloroform): 1 739, 1 731, 1 250, 1 034, 947 cm^{-1}. For $C_{34}H_{56}O_5$ (544·8) calculated: 74·95% C, 10·36% H; found: 74·67% C, 10·31% H.

b) *m*-Chloroperoxybenzoic acid (100 mg) was added to a solution of 4,4-dimethyl-A-homo-5-cholestene-3β,4aα-diol 3,4-diacetate (*XXIII*), ref.[13] (100 mg) in chloroform (5 ml) and the mixture was allowed to stand at room temperature overnight. After pouring it into water it was

extracted with ether and the extract washed with a saturated aqueous potassium hydrogen carbonate solution and water, dried over sodium sulfate and the solvent evaporated under reduced pressure. The residue (100 mg) was submitted to thin-layer chromatography on 2 preparative silica gel plates in light petroleum–ether (9 : 1), affording 90 mg of epoxide *XI* which was crystallized from methanol (73 mg), m.p. 129—131°C.

c) Diol *XII* (40 mg) was acetylated with acetic anhydride (0·2 ml) in pyridine (2 ml) at 30°C for 4 days. The conventional work-up afforded 40 mg of a crude product which was purified by preparative thin-layer chromatography on one silica gel plate in light petroleum–ether (9 : 1). Yield, 35 mg of diacetoxy derivative *XI*, which was crystallized from methanol (23 mg), m.p. 129—131°C.

4,4-Dimethyl-5,6β-epoxy-A-homo-5β-cholestane-3β,4aα-diol (*XII*)

m-Chloroperoxybenzoic acid (100 mg) was added to a solution of 4,4-dimethyl-A-homo-5-cholestene-3β,4aα-diol (*XXVII*), ref.[13], (100 mg) in chloroform (5 ml) and the mixture allowed to stand at room temperature for 1 h. After pouring it into water it was extracted with ether and the extract washed with a saturated aqueous potassium carbonate solution and water, dried over sodium sulfate and the solvent evaporated under reduced pressure. The residue (100 mg) was crystallized from dioxane–methanol. Yield, 87 mg of epoxide *XII*, m.p. 126—128°C, $[\alpha]_D^{20}$ = = +12° (*c* 0·5). Infrared spectrum (chloroform): 3 634, 1 058, 1 043, 943 cm^{-1}. Infrared spectrum (tetrachloromethane): 3 638·5, 3 503 cm^{-1}. For $C_{30}H_{52}O_3$ (460·7) calculated: 78·20% C, 11·38% H; found: 77·93% C, 11·12% H.

4,4-Dimethyl-5,6β-epoxy-A-homo-5β-cholestane-3β,4aα-diol 3-Acetate (*XIII*)

m-Chloroperoxybenzoic acid (170 mg) was added to a solution of 3-acetate *II*, ref.[13] (170 mg), in chloroform (7 ml), and the mixture was allowed to stand at room temperature for 1 h. After pouring into water it was extracted with ether and the extract washed with a saturated aqueous potassium carbonate solution and water. After drying over sodium sulfate and filtration the filtrate was evaporated under reduced pressure. The residue (170 mg) was crystallized from methanol to give 99 mg of epoxide *XIII*, m.p. 138—140°C, $[\alpha]_D^{20}$ = +12° (*c* 0·5). Infrared spectrum: 3 608, 1 734, 1 252, 1 242 cm^{-1}. ^{1}H NMR spectrum (200 MHz): 0·63 (s, 18-CH_3); 0·86 (d, 26 + 27-CH_3, J = 6·6 Hz); 0·88 (d, 21-CH_3, J = 6·3 Hz); 0·97, 1·10, 1·11 (s, 19-CH_3; s, 4,4-dimethyl); 2·12 (s, acetate); 2·92 (d, 4aα-H, $J_{4a\alpha,OH}$ = 4·8 Hz); 2·96 (d, 6α-H, $J_{6\alpha,7\beta}$ = 2·0 Hz); 4·83 (t, 3α-H, $J_{3\alpha,2\alpha} = J_{3\alpha,2\beta}$ = 3·7 Hz); For $C_{32}H_{54}O_4$ (502·7) calculated: 76·44% C, 10·83% H; found: 76·32% C, 10·79% H.

4,4-Dimethyl-5,6β-epoxy-A-homo-5β-cholestane-3β,4aβ-diol 3,4a-Diacetate (*XIV*)

a) Alcohol *XIII* (230 mg) was acetylated with acetic anhydride (6 ml) in pyridine (13 ml) for 4 days. The conventional work-up gave 230 mg of a product which was chromatographed on 5 preparative thin-layer plates (silica gel) in light petroleum–ether (9 : 1). The working up of corresponding zones gave 141 mg of diacetoxy derivative *XIV*, which was crystallized from methanol (106 mg), m.p. 162—164°C, $[\alpha]_D^{20}$ = −10° (*c* 0·5). Infrared spectrum: 1 745, 1 235, 1 022, 978, 969, 948 cm^{-1}. ^{1}H NMR spectrum (200 MHz): 0·62 (s, 18-CH_3); 0·84 (d, 21 + + 26 + 27-CH_3, J = 6·0 Hz); 0·90, 1·00, 1·04 (s, 19-CH_3; s, 4,4-dimethyl); 2·03 (s, acetate); 3·10 (d, 6α-H, $J_{6\alpha,7\beta}$ = 2·3 Hz); 4·37 (s, 4aα-H); 4·80 (mt, 3α-H). For $C_{34}H_{56}O_5$ (544·8) calculated: 74·95% C, 10·36% H; found: 74·68% C, 10·28% H. Working up of the combined more polar

zones gave 70 mg of the starting alcohol *XIII* which was crystallized from methanol (51 mg), m.p. 138–140°C, $[\alpha]_D^{20} = +12°$ (*c* 0·5).

b) Diol *XV* (40 mg) was acetylated with acetic anhydride (1 ml) in pyridine (4 ml) for 4 days. The conventional work-up gave 38 mg of a crude product which was separated preparatively on 1 thin-layer plate with silica gel in light petroleum–ether (9 : 1). Working up of the corresponding least polar zone afforded 14 mg of diacetoxy derivative *XIV* which was crystallized from methanol (6 mg), m.p. 162–164°C, $[\alpha]_D^{20} = -10°$ (*c* 0·5). Working up of the more polar zone afforded 16 mg of acetoxy derivative *XIII* which was crystallized from methanol (8·5 mg), m.p. 138–140°C, $[\alpha]_D^{20} = +12°$ (*c* 0·5). Working up of the most polar zone gave 7 mg of the starting diol *XV* which was crystallized from methanol (3 mg), m.p. 180–182°C.

c) *m*-Chloroperoxybenzoic acid (45 mg) was added to a solution of 4,4-dimethyl-A-homo-5-cholestene-3β,4aβ-diol 3,4a-diacetate (*XXIV*), ref.[13] (45 mg), in chloroform (3 ml) and the mixture was allowed to stand at room temperature overnight. After pouring into water it was extracted with ether and the extract washed with a saturated aqueous potassium carbonate solution and water, dried over sodium sulfate and evaporated under reduced pressure. The residue (43 mg) was submitted to preparative chromatography on a silica gel thin-layer plate in light petroleum–ether (9 : 1), to yield 40 mg of epoxide *XIV*, which was crystallized from methanol (29 mg), m.p. 162–164°C, $[\alpha]_D^{20} = -10°$ (*c* 0·5).

4,4-Dimethyl-5,6β-epoxy-A-homo-5β-cholestane-3β,4aβ-diol (*XV*)

An aqueous solution of potassium hydroxide (100 mg, 1 ml) was added to a solution of acetoxy derivative *XIII* (80 mg) in methanol (5 ml) and the mixture was refluxed for 1 h. After pouring into water it was extracted with ether and the extract washed with water, dried over sodium sulfate and the solvent evaporated under reduced pressure. The residue (75 mg) was crystallized from methanol to give 50 mg of diol *XV*, m.p. 180–182°C, $[\alpha]_D^{20} = 0°$ (*c* 0·5). Infrared spectrum (chloroform): 3 615, 1 049 cm^{-1}. For $C_{30}H_{52}O_3$ (460·7) calculated: 78·20% C, 11·38% H; found: 77·89% C, 11·16% H.

4,4-Dimethyl-3α-hydroxy-A-homo-5-cholesten-4a-one 3-Acetate (*XVI*)

a) Chromium trioxide (230 mg) was added to a solution of 4,4-dimethyl-A-homo-5-cholestene-3α,4aα-diol 3-acetate (*III*), ref.[13] (230 mg), in pyridine (20 ml) and the mixture was allowed to stand at room temperature overnight. The conventional work-up afforded 220 mg of a crude product which was chromatographed on 4 preparative silica gel thin-layer plates. The corresponding least polar zones afforded 80 mg of ketone *XVI*, which was crystallized from methanol (56 mg), m.p. 89–91°3C, $[\alpha]_D^{20} = -99°$ (*c* 0·5). Infrared spectrum: 1 742, 1 237, 1 030, 1 691, 3 080, 3 030, 1 660 cm^{-1}. ^1H NMR spectrum (60 MHz): 0·67 (s, 18-CH_3); 0·85 (d, 26 + 27-CH_3, $J = 6$ Hz); 0·92 (d, 21-CH_3, $J = 6$ Hz); 0·98, 1·13, 1·24 (s, 19-CH_3; s, 4,4-dimethyl); 2·04 (s, acetate); 4·64 (mt, 3β-H); 5·42 (mt, 6-H). CD spectrum (dioxane): $\Delta\varepsilon_{308} = -2·57$. For $C_{32}H_{52}O_3$ (484·7) calculated: 79·28% C, 10·81% H; found: 79·23% C, 10·62% H.

b) Chromium trioxide (60 mg) in pyridine (6 ml) was added to a solution of 4,4-dimethyl-A-homo-5-cholestene-3α,4aβ-diol 3-acetate *IV*, ref.[13] (60 mg) in pyridine (6 ml) and the reaction mixture was allowed to stand at room temperature overnight. The conventional work-up afforded 58 mg of a crude product which was chromatographed on one preparative silica gel thin-layer plate in light petroleum–ether (8 : 2). The corresponding zone was worked up to give 51 mg of ketone *XVI* which was crystallized from methanol (28 mg), m.p. 89–91°C, $[\alpha]_D^{20} = -99°$ (*c* 0·5).

c) Jones's reagent (0·5 ml) was added to a solution of alcohol *IV*, ref.[13] (30 mg), in acetone (3 ml) and the mixture allowed to stand at room temperature for 5 min under occasional shaking. After pouring into water it was extracted with ether and the extract washed with 5% potassium carbonate in water and water, then dried over sodium sulfate and the solvent evaporated under reduced pressure. The residue (28 mg) gave after preparative chromatography on one silica gel thin-layer plate 23 mg of ketone *XVI* which was crystallized from methanol (11 mg), m.p. 89–91°C, $[\alpha]_D^{20} = -99°$ (*c* 0·5).

4,4-Dimethyl-5,6β-epoxy-A-homo-5β-cholestane-3α,4aα-diol 3-Acetate (*XVII*)

a) The combined corresponding more polar zones after separation of ketone *XVI* in the preceding experiment (under *a*) were worked up to give 99 mg of epoxide *XVII* which was crystallized from methanol (56 mg), m.p. 110–112°C, $[\alpha]_D^{20} = -10°$ (*c* 0·5). Infrared spectrum (chloroform): 3 475, 1 655, 1 730, 1 255, 1 029 cm^{-1}. ^1H NMR spectrum (200 MHz): 0·65 (s, 18-CH_3); 0·86 (d, 26 + 27-CH_3, $J = 6·6$ Hz); 0·89 (d, 21-CH_3, $J = 5·9$ Hz); 0·87, 0·90, 1·06 (s, 19-CH_3; s, 4,4-dimethyl); 2·05 (s, acetate); 3·41 (d, 6α-H, $J_{6\alpha,7\beta} = 2·2$ Hz); 3·73 (s, 4aβ-H); 4·57 (dd, 3β-H, $J_{3\beta,2\alpha} = 8·7$ Hz, $J_{3\beta,2\beta} = 5·7$ Hz). For $C_{32}H_{54}O_4$ (502·75) calculated: 76·44% C, 10·83% H; found: 77·00% C, 10·73% H.

b) *m*-Chloroperoxybenzoic acid (80 mg) was added to a solution of olefin *III*, ref.[13] (80 mg) in chloroform (6 ml) and the mixture was allowed to stand at room temperature for 1 h. After pouring into water the mixture was extracted with ether and the extract washed with a saturated aqueous potassium carbonate solution and water, dried over sodium sulfate and evaporated under reduced pressure. The residue (80 mg) was chromatographed on 1 silica gel plate to give 72 mg of epoxide *XVII* which was crystallized from methanol (43 mg), m.p. 110–112°C, $[\alpha]_D^{20} = -10°$ (*c* 0·5).

3α-Acetoxy-4,4-dimethyl-5,6β-epoxy-A-homo-5β-cholestan-4a-one (*XVIII*)

a) The corresponding combined most polar zones after separation of ketone *XVI* and epoxide *XVII* in preceding experiments (under *a*) were worked up, affording 50 mg of keto epoxide *XVIII* which resisted all the attempts at crystallization, $[\alpha]_D^{20} = -112°$ (*c* 0·5). Infrared spectrum (chloroform): 1 734, 1 250, 1 031, 1 705, 967, 911 cm^{-1}. ^1H NMR spectrum (100 MHz): 0·64 (s, 18-CH_3); 0·87 (d, 26 + 27-CH_3, $J = 6·6$ Hz); 0·91 (d, 21-CH_3, $J = 6·2$ Hz); 0·99, 1·08, 1·24 (s, 19-CH_3, s, 4,4-dimethyl); 2·16 (s, acetate); 3·28 (d, 6α-H, $J_{6\alpha,7\beta} = 2·0$ Hz); 5·02 (mt, 3β-H, $\Sigma J = 11$ Hz). CD spectrum (dioxane): $\Delta\varepsilon_{302} = -3·53$. For $C_{32}H_{52}O_4$ (500·7) calculated: 76·75% C, 10·47% H; found: 76·65% C, 10·32% H.

b) Chromium trioxide (40 mg was added to a solution of alcohol *XVII* (50 mg) in pyridine (2 ml) and the mixture was allowed to stand at room temperature for 2 days. The conventional work-up gave 48 mg of a crude product which was submitted to preparative thin-layer chromatography on one silica gel plate. The required less polar zone was worked up to afford 11 mg of the starting alcohol *XVII* which was crystallized from methanol. Yield, 5 mg, m.p. 110–112°C. Working up of the more polar zone gave 32 mg of keto epoxide *XVIII*, $[\alpha]_D^{20} = -112°$ (*c* 0·5).

c) *m*-Chloroperoxybenzoic acid (40 mg) was added to a solution of olefin *XVI* (40 mg) in chloroform (2 ml) and the mixture was allowed to stand at room temperature for 3 h. After pouring into water the mixture was extracted with ether and the extract washed with a saturated aqueous potassium carbonate solution and water, then dried over sodium sulfate and the solvent evaporated under reduced pressure. The residue (39 mg) was chromatographed on a preparative silica gel

thin-layer plate. The less polar zone was worked up to give 10·5 mg of the starting olefin *XVI*, which was crystallized from methanol, m.p. 89–91°C. Working up of the more polar zone gave 26 mg of keto epoxide *XVIII*, $[\alpha]_D^{20} = -112°$ (*c* 0·5).

d) Jones's reagent (0·5 ml) was added to a solution of alcohol *III*, ref.[13] (50 mg), in acetone (3 ml) and the mixture was allowed to stand at room temperature for 5 min under occasional shaking. After pouring into water the solution was extracted with ether and the extract washed with a 5% solution of potassium hydrogen carbonate and water, dried over sodium sulfate, and the solvent evaporated under reduced pressure. The residue (45 mg) was chromatographed on one preparative thin-layer plate (silica gel), yielding 39 mg of keto epoxide *XVIII*, $[\alpha]_D^{20} = -112°$ (*c* 0·5).

e) Chromium trioxide (40 mg) was added to a solution of alcohol *XX* (50 mg) in pyridine (3 ml) and the mixture allowed to stand at room temperature overnight. The conventional work-up afforded 48 mg of a crude product which was chromatographed on a preparative silica gel thin-layer plate. The required zone was worked up to give 39 mg of keto epoxide *XVIII*, $[\alpha]_D^{20} = -112°$ (*c* 0·5).

4,4-Dimethyl-5,6β-epoxy-A-homo-5β-cholestane-3α,4aα-diol 3,4a-Diacetate (*XIX*)

a) Alcohol *XVII* (25 mg) was acetylated with acetic anhydride (0·3 ml) in pyridine overnight. The conventional work-up afforded 25 mg of a product which was chromatographed on one preparative silica gel thin-layer plate (10 × 20 cm). The required zone was worked up to give 20 mg of diacetoxy derivative *XIX*, which was crystallized from methanol, m.p. 204–206°C, $[\alpha]_D^{20} = 0°$ (*c* 0·5). Infrared spectrum: 1 751, 1 233 cm^{-1}. ^1H NMR spectrum (200 MHz): 0·62 (s, 18-CH_3); 0·858, 0·862 (d, 26-CH_3; d, 27-CH_3, $J = 6·6$ Hz); 0·88 (d, 21-CH_3, $J = 6·6$ Hz); 0·92, 0·97, 0·98 (s, 19-CH_3; s, 4,4-dimethyl); 2·02 (s, acetate); 2·06 (s, acetate); 3·18 (d, 6α-H, $J_{6\alpha,7\beta} = 2·5$ Hz); 4·60 (mt, 3β-H, $\Sigma J = 14·4$ Hz); 5·06 (s, 4aβ-H). For $C_{34}H_{56}O_5$ (544·8) calculated: 74·95% C, 10·36% H; found: 74·57% C, 10·28% H.

b) *m*-Chloroperoxybenzoic acid (50 mg) was added to a solution of 4,4-dimethyl-A-homo-5-cholestene-3α,4aα-diol 3,4a-diacetate (*XXV*), ref.[13] (50 mg), in chloroform (5 ml) and the mixture allowed to stand at room temperature for 1 h. The same work-up procedure as in the preceding experiment (under *b*) afforded 50 mg of a product which was separated chromatographically on a thin-layer silica gel plate in light petroleum–ether (9 : 1). The required zone was worked up, affording 40 mg of epoxide *XIX* which was crystallized from methanol (27 mg), m.p. 204 to 206°C, $[\alpha]_D^{20} = 0°$ (*c* 0·5.)

4,4-Dimethyl-5,6β-epoxy-A-homo-5β-cholestane-3α,4aβ-diol 3-Acetate (*XX*)

m-Chloroperoxybenzoic acid (50 mg) was added to a solution of 3-acetate *IV*, ref.[13] (50 mg), in chloroform (5 ml) and the mixture was allowed to stand at room temperature for 1 h. The same work-up procedure as in the preceding experiment (under *b*) afforded 50 mg of a product which was submitted to preparative thin-layer chromatography on a silica gel plate. The required zone was worked up to give 45 mg of epoxide *XX* which was crystallized from methanol (35 mg), m.p. 165–167°C, $[\alpha]_D^{20} = -34°$ (*c* 0·5). Infrared spectrum (chloroform): 1 730, 1 256, 3 625, 986, 946, 915 cm^{-1}. ^1H NMR spectrum (200 MHz): 0·62 (s, 18-CH_3); 0·861, 0·874 (d, 26-CH_3; d, 27-CH_3, $J = 6·6$ Hz); 0·89 (d, 21-CH_3), $J = 6·1$ Hz); 0·93, 1·03, 1·04 (s, 19-CH_3; s, 4,4-dimethyl); 2·03 (s, acetate); 2·88 (s, 4aα-H); 3·00 (d, 6α-H, $J_{6\alpha,7\beta} = 2·8$ Hz); 5·00 (d,, 3β-H, $J_{3\beta,2\alpha} = 8·5$ Hz, $J_{3\beta,2\beta} = 6·4$ Hz). For $C_{32}H_{54}O_4$ (502·75) calculated: 76·44% C, 10·83% H; found: 76·23% C, 10·68% H.

4,4-Dimethyl-5,6β-epoxy-A-homo-5β-cholestane-3α,4aβ-diol 3,4a-Diacetate (*XXI*)

a) Alcohol *XX* (50 mg) was acetylated with acetic anhydride (0·3 ml) in pyridine (3 ml) overnight. The conventional work-up gave 50 mg of a product which was crystallized from methanol to give 40 mg of diacetoxy derivative *XXI*, m.p. 152–154°C, $[\alpha]_D^{20} = -31°$ (*c* 0·5). Infrared spectrum (chloroform): 1 740, 1 258, 1 029, 979, 947, 918 cm^{-1}. ^1H NMR spectrum (200 MHz): 0·61 (s, 18-CH_3); 0·859, 0·864 (d, 26-CH_3; d, 27-CH_3, $J = 6·6$ Hz); 0·89 (d, 21-CH_3, $J = 6·6$ Hz); 0·88, 0·93, 1·01 (s, 19-CH_3; s, 4,4-dimethyl); 2·04 (s, acetate); 2·17 (s, acetate); 3·15 (d, 6α-H, $J_{6\alpha,7\beta} = 2·0$ Hz); 4·40 (s, 4aα-H); 4·83 (mt, 3β-H, $\Sigma J = 14·5$ Hz). For $C_{34}H_{56}O_5$ (544·8) calculated: 74·95% C, 10·36% H; found: 74·82% C, 10·79% H.

b) *m*-Chloroperoxybenzoic acid (50 mg) was added to a solution of 4,4-dimethyl-A-homo-5-cholestene-3α,4aβ-diol 3,4a-diacetate (*XXVI*), ref.[13] (50 mg) in chloroform (5 ml) and the mixture was allowed to stand at room temperature for 4 h. It was then poured into water and extracted with ether. The extract was washed with a saturated potassium carbonate solution and water and dried over sodium sulfate. After filtration the solvent was evaporated under reduced pressure and the residue (50 mg) chromatographed on a preparative silica gel thin-layer plate. Yield, 42 mg of epoxide *XXI* which was crystallized from methanol (30 mg), m.p. 152 to 154°C, $[\alpha]_0^{20} = -31°$ (*c* 0·5).

4,4-Dimethyl-5,6β-epoxy-A-homo-5β-cholestane·3α,4aβ-diol (*XXII*)

Lithium aluminium hydride was added to a solution of acetoxy derivative *XX* (150 mg) in ether (5 ml) and the mixture was allowed to stand at room temperature for 5 min. The excess hydride was decomposed with a saturated aqueous sodium sulfate solution and the mixture filtered through a small column of sodium sulfate. The filtrate was evaporated under reduced pressure to give 146 mg of a product which was crystallized from heptane. Yield, 110 mg of diol *XXII*, m.p. 197–199°C. Infrared spectrum (chloroform): 3 625, 1 025, 967, 941, 911 cm^{-1}. For $C_{30}H_{52}O_3$ (460·7) calculated: 78·20% C, 11·38% H; found: 77·95% C, 11·11% H.

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