SOLVOLYTIC REACTIONS OF EPIMERIC 3-METHANESULFONYLOXY--7-BENZOYLOXY-5α,6α-CYCLOPROPANOCHOLESTANES*

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Acetolysis of all possible configurational isomers of 3-methanesulfonyloxy-7-benzoyloxy-5α,6α--cyclopropanocholestanes is described and structure of the acetolysis products determined by spectroscopic methods. The 7-substituted derivatives show a greater propensity to elimination reactions than the 7-unsubstituted compounds.

Within the framework of investigating possible approaches to B-homosteroid derivatives we described some time ago[1] the solvolysis of 3-methanesulfonyloxy-5,6-cyclopropanocholestanes. We have found that 5β,6β-cyclopropano compounds solvolyze mainly with participation of the cyclopropane ring to give B-homosteroids whereas 5α,6α-cyclopropano derivatives react with predominant elimination of the 3-methanesulfonyl group. It was of interest whether and how the solvolysis is influenced by an oxygen functionality in the immediate vicinity of the cyclopropane ring.

The substrates for our solvolytic studies were prepared from the known[2] 5,6α--cyclopropano-5α-cholestane-3β,7α-diol 3β-acetate (*I*). One of the required methanesulfonates (*IV*) was prepared by esterification of the 3β-hydroxyl after suitable protection of the 7α-hydroxy group by the reaction sequence $I \rightarrow II \rightarrow III \rightarrow IV$. Another methanesulfonate, *VIII*, was synthesized from the monobenzoate *III* which after oxidation to ketone *V* followed by hydride reduction afforded a mixture of epimeric alcohols *III* and *VII* in the ratio 2 : 1. The 3α-alcohol *VII* was then converted with methanesulfonyl chloride to compound *VIII*. The remaining two isomeric methanesulfonates were obtained from benzoate *X* which in turn was prepared from the known[2] 3β-acetoxy-5,6α-cyclopropano-5α-cholestan-7-one (*VI*) by reduction with hydride to the 7β-hydroxy derivative *IX* as the principal product which was then benzoylated. Methanesulfonate *XII* was prepared from *X* by partial hydrolysis and mesylation ($X \rightarrow XI \rightarrow XII$), its epimer *XVI* was obtained by partial hydrolysis, oxidation, hydride reduction and mesylation ($X \rightarrow XI \rightarrow XIII \rightarrow XIV \rightarrow XVI$).

All the prepared methanesulfonates were acetolyzed by two hours' reflux with sodium acetate in acetic acid and acetic anhydride.

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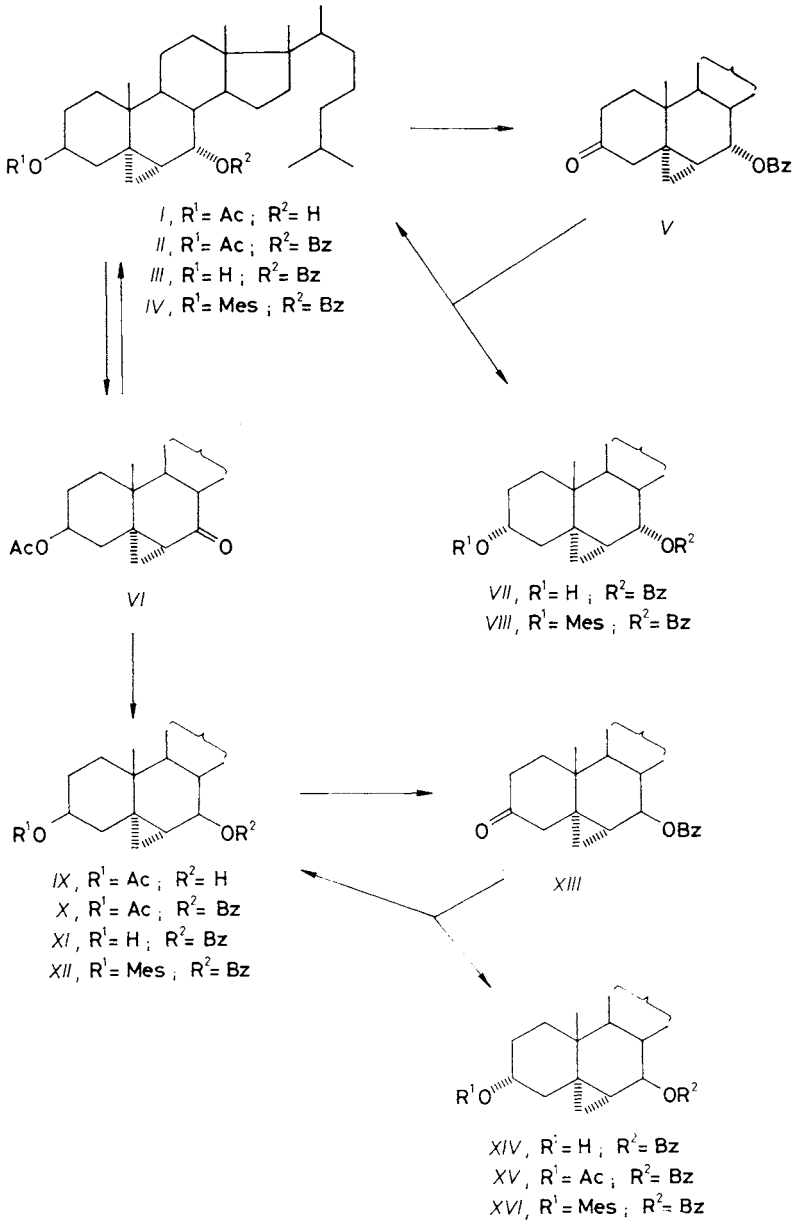
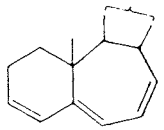
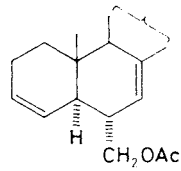
Methanesulfonates *IV* and *VIII* afford practically the same mixtures of two products (Table I). The lipophilic product *XVII* is identical with the known[3] B-homo-3,5,7--cholestatriene. The polar product contains an acetoxy group (IR spectrum: 1 742, 1 242, 1 035 cm^{-1}) and two double bonds but no cyclopropane ring (according to



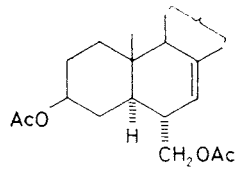
^{1}H NMR spectrum). As follows from the ^{1}H NMR spectrum, one of the double bonds is in the position 7(8) whereas the second in position 3(4). The 7-proton signal appears as a broad doublet at δ 5·47 (^3J = 4·9 Hz). The olefinic protons of the second, disubstituted, double bond are represented by two one-proton multiplets at δ 5·64 (ΣJ = 19·2 Hz) and δ 5·95 (ΣJ = 14 Hz). Since the multiplet at higher field (δ 5·64) has higher ΣJ value, it is ascribed to the $C_{(3)}$ proton (with two vicinal protons); the second multiplet (δ 5·95) belongs then to the proton at $C_{(4)}$. The spectrum exhibits also two doublets of doublets at δ 3·83 and 4·30 due to the methylene, bearing the acetoxy group (^2J = 10·4 Hz and ^3J = 8·6 Hz and 4·6 Hz). According to this evidence, the polar product has the structure *XVIII*.



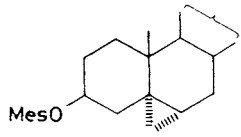
XVII



XVIII



XIX



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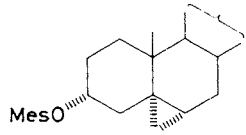

XXI

TABLE I

Solvolysis of methanesulfonates *IV*, *VIII*, *XII*, and *XVI*

Reaction	Product	Yield, %			
		IV	*VIII*	*XII*	*XVI*
Double elimination with cleavage of cyclopropane ring	*XVII*	17	18	15	19
Double elimination with addition of acetic acid to cyclopropane ring	*XVIII*	78	73	52	51
Elimination with addition of acetic acid to cyclopropane ring	*XIX*	0	0	21	16

Also the acetolysis of methanesulfonates *XII* and *XVI* affords essentially the same mixture of products (Table I). In addition to the above-obtained products *XVII* and *XVIII*, we isolated compound *XIX* which was more polar than *XVII* and *XVIII*. According to the IR spectrum (3 020, 1 733 and 1 249 cm^{-1}), this product contains an acetoxy group and a double bond but no benzoyl troup or cyclopropane ring. The ^1H NMR spectrum shows the presence of two acetoxy groups (2 singlets at δ 2·04 and 2·06). The most part of ^1H NMR spectrum is strikingly similar to that of *XVIII*, *e.g.* the doublets of doublets at δ 3·88 and 4·24 (δ 3·83 and 4·30 for *XVIII*) with coupling constants 10·6 Hz, 8·4 Hz and 4·8 Hz (for *XVIII*: 10·4 Hz, 8·6 Hz and 4·6 Hz), or the 7-proton multiplet at δ 5·48 with J = 5·2 Hz (for *XVIII*: broad doublet at δ 5·47; J = 4·9 Hz). The compound *XIX* thus contains the same $AcOCH_2$—CH—CH=C grouping as in compound *XVIII* and, in addition, a 3β-acetoxy group (the 3α-proton signal at δ 4·63; ΣJ = 32 Hz). All this evidence suggests that the compound is 3β-acetoxy-6α-acetoxymethyl-5α-cholest-7-ene.

The above-described results show that the 7-benzoyloxy group considerably influences the acetolysis of 3-methanesulfonyloxy-4,6α-cyclopropano-5α-cholestanes (Table II). Compared with analogous compounds without the oxygen functionality in position 7 (ref.[1]), the described system has significantly higher propensity to elimination reactions.

TABLE II

Acetolyses of methanesulfonates with and without 7-benzoyloxy group

Methanesulfonate	Yield		
	Substitution	Elimination	Elimination with participation of cyclopropane
7-Substituted			
IV	0	95	0
VIII	0	91	0
XII	0	88	0
XVI	0	86	0
7-Unsubstituted[a]			
XX	29	51	5
XXI	7	80	0

[a] Ref.[1].

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. Optical rotations were measured in chloroform, error $\pm 3°$. Infrared spectra were recorded on a Zeiss UR-20 spectrometer in tetrachloromethane, unless stated otherwise. ^{1}H NMR spectra were obtained with a Tesla B 476 (60 MHz) or a Varian HA 100 (100 MHz) instruments in deuteriochloroform with tetramethylsilane as internal standard (unless stated otherwise). Chemical shifts are given in the δ-scale; $W_{1/2}$ denotes signal half-width. The spectra were interpreted as first-order spectra. Mass spectra were measured on an AEI MS 902 spectrometer. The identity of the prepared samples was checked by mixture melting point determinations, thin-layer chromatography (TLC), and IR and ^{1}H NMR spectra. Preparative TLC was carried out on 200 × 200 mm plates with 0·7 mm thick layer of silica gel. „The usual work-up of the solution" means successive washing with 5% hydrochloric acid, water, 5% aqueous potassium hydrogen carbonate and water, drying over sodium sulfate, filtration and evaporation of the solvent *in vacuo*. Light petroleum was a fraction of b.p. 40–62°C.

5,6α-Cyclopropano-5α-cholestane-3β,7α-diol 3-Acetate (*I*)

Lithium tri-tert-butoxyaluminium hydride (240 mg) was added to a solution of ketone *V* (120 mg) in tetrahydrofuran (Merck, 10 ml). After standing for 8 h at room temperature, another part of the hydride (240 mg) was added. The mixture was set aside for 20 h, poured into water and the product was extracted with ether and worked up as usual. The residue consisted of two compounds of very similar R_F; it was therefore applied on three preparative TLC plates and chromatographed in ether–light petroleum (1 : 1). Zones, containing the lipophilic product, afforded 13 mg of the alcohol *I*, m.p. 152–153°C; $[\alpha]_D^{20}$ −87° (*c* 1), in accord with the published data[2].

5,6α-Cyclopropano-5α-cholestane-3β,7α-diol 3-Acetate 7-Benzoate (*II*)

Benzoyl chloride (6·6 ml) was added to a solution of alcohol *I* (ref.[2]; 1·65 g) in pyridine (19·5 ml). After standing at room temperature overnight, the mixture was poured under stirring into water at 40°C, cooled to room temperature and the product was taken up in ether. The usual work-up, followed by crystallization from methanol, afforded 650 mg of benzoate *II*, m.p. 118–120°C; $[\alpha]_D^{20}$ −100° (*c* 1·5). IR spectrum: 3 095, 3 075, 3 070, 3 035 (cyclopropane + aromatic bands), 1 735, 1 247 (acetate), 1 719, 1 278 (benzoate) cm^{-1}. ^{1}H NMR spectrum: 0·22 (dd, J = 4·5 Hz, J' = 8·5 Hz, cyclopropane protons), 0·65 (s, 18-H), 0·85 (d, J = 5·5 Hz, 26-H and 27-H), 0·91 (d, J = 5·5 Hz, 21-H), 1·17 (s, 19-H), 2·00 (s, 3-acetate), 4·78 (mt, $W_{1/2}$ = 27 Hz, 3α-H), 5·27 (mt, $W_{1/2}$ = 15 Hz, 7β-H), 7·32 to 7·66 and 7·88 to 8·22 (2 mt, 7-benzoate). For $C_{37}H_{54}O_4$ (562·8) calculated: 78·96% C, 9·67% H; found: 78·66% C, 9·63% H.

5,6α-Cyclopropano-5α-cholestane-3β,7α-diol 7-Benzoate (*III*)

a) Potassium carbonate (102 mg) was added to a solution of acetate *II* (206 mg) in methanol (20 ml) and water (0·75 ml). The mixture was briefly heated to the boil and then allowed to stand for 2 h at room temperature. After pouring into water, the product was extracted with ether and the extract was worked up in the usual manner, affording 175 mg of chromatographically pure product. Crystallization from aqueous methanol furnished 60 mg of alcohol *III*, m.p. 121–126°C with resolidification and final m.p. 167–171°C; $[\alpha]_D^{20}$ −96° (*c* 0·75). IR spectrum: 3 620 (hydroxyl), 3 070 (cyclopropane), 1 712, 1 278 (benzoate) cm^{-1}. ^{1}H NMR spectrum: −0·07 to 0·23 (mt, cyclopropane protons), 0·63 (s, 18-H), 0·83 (d, J = 5·8 Hz, 26-H and 27-H), 0·90 (d, J = 5·5 Hz, 21-H), 1·14 (s, 19-H), 3·70 (mt, $W_{1/2}$ = 27 Hz, 3α-H), 5·28 (dd, J = 5·5 Hz, J' = 8 Hz, 7β-H),

7·35 to 7·67 and 7·95 to 8·18 (2 mt, 7-benzoate). For $C_{35}H_{52}O_3$ (520·8) calculated: 80·71% C, 10·07% H; found: 80·82% C, 10·16% H.

b) Zones of the polar product from preparative TLC in the preparation of compound *VII* from ketone *V* afforded 220 mg of alcohol *III*, m.p. 167—170°C, $[\alpha]_D^{20}$ −95° (*c* 1).

5,6α-Cyclopropano-5α-cholestane-3β,7α-diol 3-Acetate 7-Methanesulfonate (*IV*)

Methanesulfonyl chloride (0·38 ml) was added at 5°C to a solution of alcohol *III* (380 mg) in pyridine (7·6 ml). After standing for 4 h at room temperature, the product was taken up in ethyl acetate and the extract processed in the usual manner, affording 395 mg of an oil, $[\alpha]_D^{20}$ −115° (*c* 1). IR spectrum: 1 716, 1 178 (benzoate), 1 346, 1 180 (methanesulfonate) cm^{-1}. ^1H NMR spectrum: 0·05 to 0·52 (mt, cyclopropane protons), 0·65 (s, 18-H), 0·86 (d, J = 5·5 Hz, 26-H and 27-H), 0·90 (d, J = 5 Hz, 21-H), 1·13 (s, 19-H), 2·93 (s, methanesulfonate), 4·72 (mt, $W_{1/2}$ = = 27 Hz, 3α-H), 5·23 (mt, $W_{1/2}$ = 16 Hz, 7β-H), 7·19 to 7·50 (mt) and 7·76 to 7·90 (mt) (7-benzoate). For $C_{36}H_{54}O_5S$ (598·9) calculated: 72·20% C, 9·09% H; found: 72·01% C, 8·89% H.

7α-Benzoyloxy-5,6α-cyclopropano-5α-cholestan-3-one (*V*)

Jones reagent[4] was added dropwise to a solution of alcohol *III* (340 mg) in acetone (10 ml) to a constant brown coloration. The mixture was set aside at room temperature for 10 min, methanol (1 ml) was added and after standing for 5 min the mixture was poured into water. The product was taken up in ether, the ethereal extract was washed with saturated potassium hydrogen carbonate solution, water and dried. Evaporation of the solvent and crystallization of the residue from acetone gave 215 mg of ketone *V*, m.p. 191—192°C, $[\alpha]_D^{20}$ −100° (*c* 1·5). IR spectrum: 3 075 (cyclopropane), 1 719 (ketone), 1 713, 1 278 (benzoate) cm^{-1}. ^1H NMR spectrum: 0·03 to 0·33 (mt, cyclopropane protons), 0·65 (s, 18-H), 0·82 (d, J = 6 Hz, 26-H and 27-H), 0·90 (d, J = 5·5 Hz, 21-H), 1·30 (s, 19-H), 2·43 (mt, $W_{1/2}$ = 13 Hz, 2-H and 4-H), 3·02 (d, J = 15 Hz, one of 4-H), 5·25 (mt, $W_{1/2}$ = 17 Hz, 7α-H), 7·31 to 7·63 and 7·86 to 8·17 (mt, benzoate). For $C_{35}H_{50}O_3$ (518·8) calculated: 81·02% C, 9.72% H; found: 81·39% C, 9·65% H.

5,6α-Cyclopropano-5α-cholestane-3α,7α-diol 7-Benzoate (*VII*)

Lithium tri-tert-butoxyaluminium hydride (1·2 g) was added to ketone *V* (580 mg) in tetrahydrofuran (30 ml). After standing for 2 h at room temperature, the excess hydride was decomposed with water, the product extracted with ether and the extract worked up as usual. The residue contained (TLC) two compounds which were separated by preparative TLC in ether–light petroleum (3 : 2). Zones, containing the lipophilic product, afforded 271 mg of oily alcohol *VII*, $[\alpha]_D^{20}$ −108° (*c* 0·7). IR spectrum: 3 620 (hydroxyl), 3 075 (cyclopropane), 1 713, 1 179 (benzoate) cm^{-1}. ^1H NMR spectrum: 0·24 to 0·52 (mt, cyclopropane protons), 0·66 (s, 18-H), 0·85 (d, J = 5·5 Hz, 26-H and 27-H), 0·91 (d, J = 5 Hz, 21-H), 1·11 (s, 19-H), 4·03 (mt, $W_{1/2}$ = 9 Hz, 3β-H), 5·35 (mt, $W_{1/2}$ = 23 Hz, 7β-H), 7·32 to 7·63 and 7·89 to 8·14 (2 mt, benzoate). For $C_{35}H_{52}O_3$ (520·8) calculated: 80·71% C, 10·07% H; found: 80·16% C, 9·87% H.

5,6α-Cyclopropano-5α-cholestane-3α,7α-diol 3-Methanesulfonate 7-Benzoate (*VIII*)

Methanesulfonyl chloride (0·32 ml) was added to a solution of alcohol *VII* (165 mg) in pyridine (2 ml). After standing overnight at room temperature, the product was extracted with ethyl acetate and worked up in the usual manner; yield 110 mg of the oily product *VIII*; $[\alpha]_D^{20}$ −66° (*c* 1·5).

IR spectrum: 3 075 (cyclopropane), 1 713, 1 278 (benzoate), 1 342, 1 180 (methanesulfonate) cm^{-1}. ^1H NMR spectrum: 0·65 (s, 18-H), 0·85 (d, J = 6 Hz, 26-H and 27-H), 0·91 (d, J = 5·5 Hz, 21-H), 1·25 (s, 19-H), 2·87 (s, methanesulfonate), 4·79 to 5·35 (overlapping multiplets 3β-H and 7β-H), 7·34 to 7·61 and 7·88 to 8·10 (two mt, benzoate). For $C_{36}H_{54}O_5S$ (598·9) calculated: 72·20% C, 9·09% H, 5·35% S; found: 72·62% C, 9·01% H, 5·30% S.

5,6α-Cyclopropano-5α-cholestane-3β,7β-diol 3-Acetate (*IX*)

Zones of polar product from TLC in the preparation of 7α-alcohol *I* afforded 75 mg of 7β-alcohol *IX*, m.p. 116–118°C, $[\alpha]_D^{20}$ −21° (*c* 1·5). IR spectrum: 3 625 (hydroxyl), 3 075 (cyclopropane), 1 738, 1 248 (benzoate) cm^{-1}. ^1H NMR spectrum: 0·10 to 0·33 and 0·40 to 0·56 (two mt, cyclopropane protons), 0·66 (s, 18-H), 0·87 (d, J = 6 Hz, 26-H and 27-H), 0·90 (d, J = 6·5 Hz, 21-H), 1·16 (s, 19-H), 2·01 (s, 3β-acetate), 3·73 (mt, J = 9 Hz, 7α-H), 4·79 (mt, $W_{1/2}$ = 27 Hz, 3α-H). For $C_{30}H_{50}O_3$ (458·7) calculated: 78·55% C, 10·99% H; found: 78·74% C, 10·45% H.

5,6α-Cyclopropano-5α-cholestane-3β,7β-diol 3-Acetate 7-Benzoate (*X*)

Benzoyl chloride (0·9 ml) was added to a solution of alcohol *IX* (880 mg) in pyridine (80 ml). The mixture was allowed to stand overnight and then slowly added dropwise into water at 40°C. After cooling to room temperature, the product was extracted with ether and worked up as usual. The obtained residue (1 g) was purified by chromatography on a column of silica gel (200 g) in ether–light petroleum (3 : 17); yield 920 mg of an oil; $[\alpha]_D^{20}$ −6° (*c* 1). IR spectrum: 3 075 (cyclopropane), 1 738, 1 247, 1 030 (acetate), 1 722, 1 247 (benzoate) cm^{-1}. ^1H NMR spectrum: 0·17 to 0·50 (mt, cyclopropane protons), 0·67 (s, 18-H), 0·84 (d, J = 5·8 Hz, 26-H and 27-H), 0·88 (d, J = 5·5 Hz, 21-H), 1·23 (s, 19-H), 1·98 (s, acetate), 4·82 (mt, $W_{1/2}$ = 25 Hz, 3α-H), 5·03 (d, J = 6 Hz, 7α-H), 7·36 to 7·66 and 7·89 to 8·17 (two mt, benzoate). For $C_{37}H_{54}O_4$ (562·8) calculated: 78·96% C, 9·67% H; found: 78·91% C, 9·71% H.

5,6α-Cyclopropano-5α-cholestane-3β,7β-diol 7-Benzoate (*XI*)

a) Potassium carbonate (550 mg) was added to a solution of compound *X* (458 mg) in methanol (55 ml) and water (5·5 ml). The mixture was stirred for 3·5 h at room temperature, poured into water and the product was extracted with ether. The organic layer was separated, washed with water, dried and the solvent evaporated. Chromatography of the residue on a column of silica gel (100 g) in ether–light petroleum (3 : 7) afforded 320 mg of alcohol *XI*; $[\alpha]_D^{20}$ +32° (*c* 1·6). IR spectrum: 3 625 (hydroxyl), 3 075 (cyclopropane), 1 715, 1 277 (benzoate) cm^{-1}. ^1H NMR spectrum: 0·08 to 0·41 (mt, cyclopropane protons), 0·68 (s, 18-H), 0·85 (d, J = 5·5 Hz, 26-H and 27-H), 0·89 (d, J = 5·0 Hz, 21-H), 1·23 (s, 19-H), 3·69 (mt, $W_{1/2}$ = 21 Hz, 3α-H), 5·02 (d, J = 6 Hz, 7α-H), 7·38 to 7·63 and 7·92 to 8·20 (two mt, benzoate). For $C_{35}H_{52}O_3$ (520·8) calculated: 80·71% C, 10·07% H; found: 80·39% C, 9·98% H.

b) Lithium tri-tert-butoxyaluminium hydride (1·2 g) was added to a solution of ketone *XIII* (600 mg) in tetrahydrofuran (Merck, 12 ml). After standing for 8 h at room temperature, the mixture was poured into water, extracted with ether and the extract processed in the usual manner. The obtained product, consisting of two compounds of very similar R_F, was chromatographed on a column of silica gel (150 g) in ether–light petroleum (1 : 4) to remove most of the polar product (420 mg). The fraction, containing both compounds (50 mg), was further purified by preparative TLC (2 plates) in ether–light petroleum (2 : 3). Zones with the lipophilic product afforded 35 mg of alcohol *XI*, $[\alpha]_D^{20}$ +30° (*c* 1).

5,6α-Cyclopropano-5α-cholestane-3β,7β-diol 3-Methanesulfonate 7-Benzoate (*XII*)

Methanesulfonyl chloride (1·7 ml) was added to a solution of alcohol *XI* (1·7 g) in pyridine (8 ml). After standing for 2·5 h at room temperature, the mixture was poured into water, extracted with ethyl acetate and the extract worked up rapidly in the usual manner; yield 1·9 g of an oil, $[\alpha]_D^{20}$ +6° (*c* 5). IR spectrum: 3 075 (cyclopropane), 1 719, 1 714, 1 276 (benzoate), 1 344, 1 179 (methanesulfonate) cm^{-1}. Mass spectrum *m/z*: 598 (M), 502 (M − CH_3SO_3H), 476 (M − C_6H_5COOH), 461 (M − C_6H_5COOH − CH_3), 380 (base peak, M − CH_3SO_3H − C_6H_5COOH). ^1H NMR spectrum: 0·11 to 0·48 (mt, cyclopropane protons), 0·67 (s, 18-H), 0·84 (d, J = 6 Hz, 26-H and 27-H), 0·89 (d, J = 5·5 Hz, 21-H), 1·26 (s, 19-H). For $C_{36}H_{54}O_4S$ (598·9) calculated: 72·20% C, 9·09% H; found: 72·45% C, 8·99% H.

7β-Benzoyloxy-5,6α-cyclopropano-5α-cholestan-3-one (*XIII*)

Jones reagent[4] was added to a solution of alcohol *XI* (180 mg) in acetone (5 ml) to a constant brown coloration, and the mixture was set aside for 10 min at room temperature. Methanol (0·5 ml) was added and after 5 min the mixture was poured into water. The product was taken up in ether, the organic phase washed with 10% solution of potassium hydrogen carbonate, dried and the solvent distilled off. Crystallization of the residue (160 mg) from methanol afforded 119 mg of ketone *XIII*, m.p. 140—143°C; $[\alpha]_D^{20}$ +64° (*c* 0·8). IR spectrum: 3 070 (cyclopropane), 1 720, 1 276 (benzoate), 1 713 (3-ketone) cm^{-1}. ^1H NMR spectrum: 0·14 to 0·50 (mt, cyclopropane protons), 0·72 (s, 18-H), 0·85 (d, J = 5·7 Hz, 26-H and 27-H), 0·93 (d, J = 5 Hz, 21-H), 1·42 (s, 19-H), 2·21 to 2·65 (mt) and 3·03 (d, J = 15·5 Hz) (2-H and 4-H), 5·02 (d, J = 6·5 Hz, 7α-H), 7·39 to 7·64 and 7·92 to 8·19 (two mt, benzoate). For $C_{35}H_{50}O_3$ (518·8) calculated: 81·02% C, 9·72% H; found: 81·74% C, 9·59% H.

5,6α-Cyclopropano-5α-cholestane-3α,7β-diol 7-Benzoate (*XIV*)

Zones of the polar product from the preparative TLC in the preparation of 3β-alcohol *XI* according to *b*) were combined, the product was eluted with ether and combined with the polar product obtained by column chromatography in the preparation of *XI*, described *ad b*). Total yield 435 mg of 3α-alcohol *XIV* (oil); $[\alpha]_D^{20}$ +25° (*c* 1·6). IR spectrum: 3 625, 1 048 (hydroxyl), 3 070 (cyclopropane), 1 716, 1 276 (benzoate) cm^{-1}. ^1H NMR spectrum: 0·08 to 0·44 (mt, cyclopropane protons), 0·70 (s, 18-H), 0·87 (d, J = 5·5 Hz, 26-H and 27-H), 0·90 (d, J = 5 Hz, 21-H), 1·25 (s, 19-H), 3·69 (mt, $W_{1/2}$ = 14 Hz, 3β-H), 5·09 (d, J = 6 Hz, 7α-H), 7·33 to 7·71 and 8·02 to 8·31 (two mt, benzoate). For $C_{35}H_{52}O_3$ (520·8) calculated: 80·71% C, 10·07% H; found: 80·62% C, 10·15% H.

5,6α-Cyclopropano-5α-cholestane-3α,7β-diol 3-Acetate 7-Benzoate (*XV*)

A solution of alcohol *XIV* (70 mg) in pyridine (1 ml) and acetic anhydride (0·6 ml) was set aside at room temperature overnight, poured into water, the product was taken up in ether and worked up as usual. Yield 73 mg of oily *XV*; $[\alpha]_D^{20}$ +7° (*c* 5·6). IR spectrum: 3 075 (cyclopropane), 1 732, 1 247 (acetate), 1 718, 1 275 (benzoate) cm^{-1}. ^1H NMR spectrum: 0·15 to 0·50 (mt, cyclopropane protons), 0·68 (s, 18-H), 0·85 (d, J = 6 Hz, 26-H and 27-H), 0·89 (d, J = 5 Hz, 21-H), 1·23 (s, 19-H), 1·97 (s, 3-acetate), 4·73 (mt, $W_{1/2}$ = 23 Hz, 3β-H), 4·99 (mt, J = 7 Hz, 7α-H), 7·29 to 7·60 and 7·87 to 8·16 (two mt, benzoate). For $C_{37}H_{54}O_4$ (562·8) calculated: 78·96% C, 9·67% H; found: 78·42% C, 9·35% H.

5,6α-Cyclopropano-5α-cholestane-3α,7β-diol 3-Methanesulfonate 7-Benzoate (*XIV*)

Methanesulfonyl chloride (0·5 ml) was added to a solution of alcohol *XV* (0·38 g) in pyridine (5 ml). After standing for 3 h at room temperature the mixture was poured into water, extracted with ethyl acetate and the extract worked up as rapidly as possible in the usual manner to afford 360 mg of light yellow oil, $[\alpha]_D^{20}$ +10° (*c* 0·6). IR spectrum: 1 719, 1 279 (benzoate), 1 347, 1 181 (methanesulfonate) cm^{-1}. ^1H NMR spectrum: 0·18 to 0·58 (mt, cyclopropane protons), 0·67 (s, 18-H), 0·83 (d, J = 5 Hz, 26-H and 27-H), 0·89 (d, J = 5 Hz, 21-H), 1·25 (s, 19-H), 2·90 (s, 3-methanesulfonate), 4·60 to 5·15 (mt, 7α-H), 7·23 to 7·52 and 7·82 to 8·13 (two mt, benzoate). Mass spectrum *m/z*: 598 (M), 502 (M − CH_3SO_3H), 476 (M − C_6H_5COOH), 461 (M − C_6H_5·.COOH − CH_3), 380 (base peak, M − C_6H_5COOH − CH_3SO_3H). For $C_{36}H_{54}O_5S$ (598·9) calculated: 72·20% C, 9·09% H, 5·35% S; found: 72·13% C, 9·00% H, 5·60% S.

B-Homocholesta-3,5,7-triene (*XVII*)

a) Methanesulfonate *IV* (370 mg), fused anhydrous sodium acetate (400 mg), acetic acid (15 ml) and acetic anhydride (1·5 ml) were mixed together in the given order. The mixture was refluxed for 2 h under nitrogen (air condenser), cooled and poured into water. The product was taken up in diethyl ether and the organic layer was washed with water, saturated potassium hydrogen carbonate solution, water, and dried. The solution was evaporated and the product purified by preparative TLC (8 plates) in ether–light petroleum (1 : 33). Fractions with the lipophilic product gave 41 mg of chromatographically pure oil which crystallized on standing at −18°C. Crystallization from methanol afforded 8 mg of triene *XVII*, m.p. 70–72°C (decomposition); $[\alpha]_D^{20}$ −435° (*c* 1), in accord with the published values[3].

b) A mixture of methanesulfonate *VIII* (40 mg), sodium acetate (40 mg), acetic acid (1·5 ml) and acetic anhydride (0·15 ml) was treated and worked up in the same manner as described in the experiment *a*), affording 4·5 mg of triene *XVII* whose spectral properties were identical with those of the product prepared above.

c) A mixture of methanesulfonate *XII* (1·4 g), sodium acetate (1·0 g), acetic acid (30 ml) and acetic anhydride (3 ml) was treated as described under *a*). The obtained mixture of three products was chromatographed on a column of silica gel (100 g) in light petroleum. Fractions containing the lipophilic product afforded 130 mg of the triene, identical in all respects with the compound obtained according to procedure *a*).

d) Methanesulfonate *XVI* (415 mg) was acetolyzed in a mixture of fused sodium acetate (500 mg), acetic acid (15 ml) and acetic anhydride (1·5 ml) as described under *a*). Similar work-up furnished 380 mg of an oil which was chromatographed on a silica gel column (100 g) in light petroleum. Yield 51 mg of the triene, identical with the product obtained under *a*).

6α-Acetoxymethyl-5α-cholesta-3,7-diene (*XVIII*)

a) Zones of the polar product from TLC in the preparation of triene *XVII* according to procedure *a*) afforded 212 mg of oily *XVIII*; $[\alpha]_D^{20}$ −251° (*c* 1). IR spectrum: 3 025, 1 652 (double bond), 1 741, 1 242, 1 035 (acetate) cm^{-1}. Mass spectrum *m/z*: 440 (M), 425 (M − CH_3), 380 (M − CH_3COOH, base peak). ^1H NMR spectrum (200 MHz, Varian XL 200): 0·69 (s, 18-H), 0·98 (s, 19-H), 2·04 (s, 6-CH_2OAc), 2·40 (mt, $J_{6\beta,CH_2OAc}$ 8·6 + 4·6 Hz, $J_{6\beta,7}$ = 4·9 Hz, 6β-H), 3·83 (dd, J_{gem} = 10·4 Hz, $J_{6\beta,CH_2OAc}$ = 8·6 Hz) and 4·30 (dd, J_{gem} = 10·4 Hz, $J_{6\beta,CH_2OAc}$ = 4·6 Hz) (together: 6-CH_2OAc), 5·47 (bd, J = 4·9 Hz, 7-H), 5·64 (mt, ΣJ = 19·2 Hz, 3-H), 5·95 (mt, ΣJ = 14 Hz, 4-H). For $C_{30}H_{48}O_2$ (440·7) calculated: 81·76% C, 10·98% H; found: 81·20% C, 10·71% H.

b) Zones of the polar product from the preparation of triene *XVII* according to procedure *b*) afforded 22·5 mg of diene *XVIII*, $[\alpha]_D^{20}$ 236° (*c* 0·4), identical with the product obtained in the preceding experiment.

c) Continuation of the chromatography in the preparation of triene *XVII* according to procedure *c*) (elution with ether–light petroleum 1 : 33 and then 1 : 10) gave 535 mg of diene *XVIII*, identical in all respects with the product of experiment *a*).

d) Continuation of chromatography from the preparation of triene *XVII* according to procedure *d*) (elution with ether–light petroleum 1 : 33 and then 1 : 10) afforded 156 mg of diene *XVIII*, identical with the product prepared *ad a*).

3β-Acetoxy-6α-acetoxymethyl-5α-cholest-7-ene (*XIX*)

a) Continuation of chromatography in the preparation of diene *XVIII* according to procedure *c*) furnished 246 mg of chromatographically pure olefin *XIX* which on crystallization from methanol melted at 93·6–94·5°C (145 mg); $[\alpha]_D^{20}$ −107° (*c* 0·7). IR spectrum (KBr): 3 020 sh (double bond), 1 733, 1 249 (acetate) cm^{-1}. Mass spectrum *m/z*: 380 (base peak, M − 2 × CH_3.COOH). ^1H NMR spectrum (200 MHz; Varian XL 200): 0·66 (s, 18-H), 0·865 (d, J = 6·6 Hz) and 0·87 (d, J = 6·6 Hz) (26-H and 27-H), 0·92 (d, J = 6·5 Hz, 21-H), 1·04 (s, 19-H), 2·04 and 2·06 (two s, two acetoxy groups), 2·24 (mt, ΣJ = 24·8 Hz, J = 4·8 Hz, J' = 8·4 Hz, J'' = 5·2 Hz, J''' 6·4 Hz, 6β-H), 2·36 (d, J = 8 Hz, 9-H or 13-H), 3·88 (dd, J = 8·4 Hz, J' = 10·6 Hz) and 4·24 (dd, J 4·8 Hz, J' = 10·6 Hz) (together: 6-CH_2—OAc), 4·63 (mt, ΣJ = 32 Hz, 3α-H), 5·48 (d, J 5·2 Hz, 7-H). For $C_{32}H_{54}O_4$ (502·7) calculated: 76·44% C, 10·83% H; found: 76·39% C, 10·81% H.

b) Continuation of chromatography in the preparation of diene *XVIII* according to procedure *d*) afforded 57 mg of olefin *XIX*, m.p. 93–94°C; $[\alpha]_D^{20}$ −103° (*c* 1), identical in all respects with the product prepared by procedure *a*).

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