20. *The Dehalogenation of* 6-*Chloro*-3-*benzoyloxy*-Δ^4-*cholestene.*

By F. S. Spring and G. Swain.

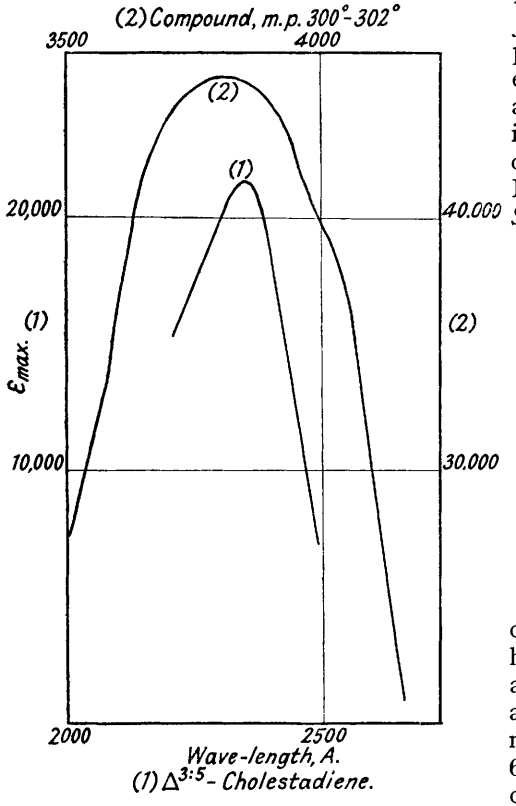
Attempts have been made to dehydrate β-cholesteryl benzoate oxide; on pyrolysis it is isomerised in part with production of the α-benzoate oxide. 6-Chloro-3-benzoyloxy-Δ^4-cholestene (I), which is obtained from the α-oxide by treatment with hydrochloric acid, when reduced with aluminium amalgam gives $\Delta^{3:5}$-cholestadiene in high yield, replacement of the halogen atom having been accompanied by loss of benzoic acid. When treated with potassium acetate, 6-chloro-3-benzoyloxy-Δ^4-cholestene (I) gives a mixture of three halogen-free products, two of which are isomeric and have been identified as benzoate monoethyl ethers of either 3 : 4-dihydroxy-Δ^5-cholestene (V) or 3 : 6-dihydroxy-Δ^4-cholestene (II, R = R′ = H). The third product is a monobenzoate of *cis*-3 : 4-dihydroxy-Δ^5-cholestene (V), which differs from the monobenzoate of the *cis*-diol previously described by Rosenheim and Starling. During the formation of one of the monobenzoates of the *cis*-diol, a migration of a benzoyl group from C_3 to C_4 has occurred.

We have previously reported upon the preparation and some properties of α- and β-cholesteryl benzoate oxides (Spring and Swain, J., 1939, 1356), a study instigated by the fact that dehydration of 2-methyl-Δ^1-butene oxide gives isoprene (Kyriakides, *J. Amer. Chem. Soc.*, 1914, **36**, 663); it was hoped that under suitable reaction conditions dehydration of cholesteryl ester oxides would lead either to the corresponding ester of 7-dehydrocholesterol or to that of $\Delta^{4:6}$-cholestadienol. When heated with either phosphoric oxide or dehydrated alum, α-cholesteryl benzoate oxide is isomerised to 6-ketocholestanyl benzoate; the oxide is stable to prolonged heating at 270°/13 mm., and is likewise unaffected by treatment with thionyl chloride in pyridine and by heating under reflux with dimethylaniline. β-Cholesteryl benzoate oxide also is unaffected by prolonged heating with dimethylaniline and by treatment with thionyl chloride in pyridine. It is, however, less stable to heat treatment than its α-isomer; after heating for a short time at 270°/13 mm., benzoic acid sublimed and the residue was resolved into α-cholesteryl benzoate oxide and a *compound*, m. p. 300—302°. α-Cholesteryl benzoate oxide has now been prepared by four different methods, *viz.*, treatment of cholesteryl benzoate with perbenzoic acid, by the removal of hydrogen chloride from 6-chloro-5-hydroxy-3-benzoyloxycholestane, by treatment of 3 : 5 : 6-trihydroxycholestane with benzoic anhydride (Spring and Swain, *loc. cit.*), and now by isomerisation of the β-oxide. In each case the product has m. p. 168—169°, $[\alpha]_D$ − 31°; the product, m. p. 181°, described by Lettré and Müller (*Ber.*, 1937, **70**, 1947) as α-cholesteryl benzoate oxide is either a mixture or is incorrectly described.

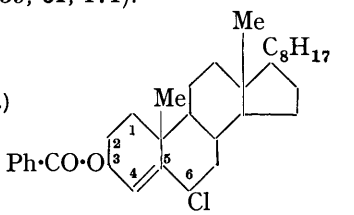
Analysis and molecular weight determinations of the compound, m. p. 300—302° (which is obtained in very small yield), indicate a molecular formula of the type $(C_{27}H_{42}O)_3$. It exhibits an intense absorption maximum at 3825 A. (Fig.) and does not contain active

hydrogen (Zerewitinoff). The amount of this substance available was not sufficient for further examination.

In view of this failure to dehydrate the cholesteryl benzoate oxides in the desired manner, attention was next directed to the removal of hydrogen chloride from 6-chloro-3-benzoyloxy-Δ^4-cholestene (I), previously obtained by us from α-cholesteryl benzoate oxide (*loc. cit.*). In order further to characterise this intermediate it was reduced with aluminium amalgam in moist ether. Instead of the expected *allo*cholesteryl benzoate (3-benzoyloxy-Δ^4-cholestene) a cholestadiene, $C_{27}H_{44}$, m. p. 80—81°, $[\alpha]_D$ — 129·6°, was obtained in high yield. An examination of the spectrum of this hydrocarbon by Dr. A. E. Gillam (to whom we are also indebted for the previously mentioned absorption spectrum) has shown it to possess an intense absorption maximum at 2350 A. (Fig.); the location of the absorption maximum and the strong lævorotation indicate that the hydrocarbon is $\Delta^{3:5}$-cholestadiene (Stavely and Bergmann, *J. Org. Chem.*, 1937, **1**, 567). In physical properties it closely resembles the cholestadienes obtained by the action of hydrochloric acid upon a mixture of *allo*cholesterol and its epimeride and by the pyrolysis of cholesteryl methyl xanthogenate (Eck, Van Peursem, and Hollingsworth, *J. Amer. Chem. Soc.*, 1939, **61**, 171).



(I.)



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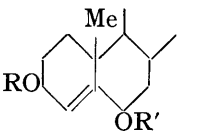


Treatment of 6-chloro-3-benzoyloxy-Δ^4-cholestene with methyl-alcoholic potassium hydroxide or sodium methoxide gave unworkable oils; when heated with pyridine, it gave a chlorine-free resinous product which could not be crystallised. The halogen atom of 6-chloro-3-benzoyloxy-Δ^4-cholestene was successfully removed when the compound was heated with potassium acetate in alcohol, a mixture being obtained which was resolved into three products: (A), m. p. 166—167°, $[\alpha]_D$ — 47·2°; (B), m. p. 131—132°, $[\alpha]_D$ — 29·4°, and (C), m. p. 153—154°, $[\alpha]_D$ — 27·8°.

Analysis of compound (C) shows that it has the formula $C_{34}H_{50}O_3$, that it has been formed by replacement of the chlorine atom of 6-chloro-3-benzoyloxy-Δ^4-cholestene by a hydroxyl group, and suggests that it is either 6-hydroxy-3-benzoyloxy-Δ^4-cholestene (II; R = COPh, R' = H) or 4-hydroxy-3-benzoyloxy-Δ^5-cholestene (III); in the former, simple replacement of the halogen in (I) by hydroxyl is assumed and in the latter this replacement has been accompanied by an allylic rearrangement. 4-Hydroxy-3-benzoyloxy-Δ^5-cholestene (III) has been prepared by Rosenheim and Starling (J., 1937, 377) by partial esterification of *cis*-3 : 4-dihydroxy-Δ^5-cholestene (V) and by oxidation of cholesteryl benzoate with selenium dioxide; it has m. p. 209—210°, $[\alpha]_D$ — 30·7°, and is markedly different from the compound (C). In order further to characterise compound (C), it was hydrolysed in the expectation that 3 : 6-dihydroxy-Δ^4-cholestene (II; R = R' = H)

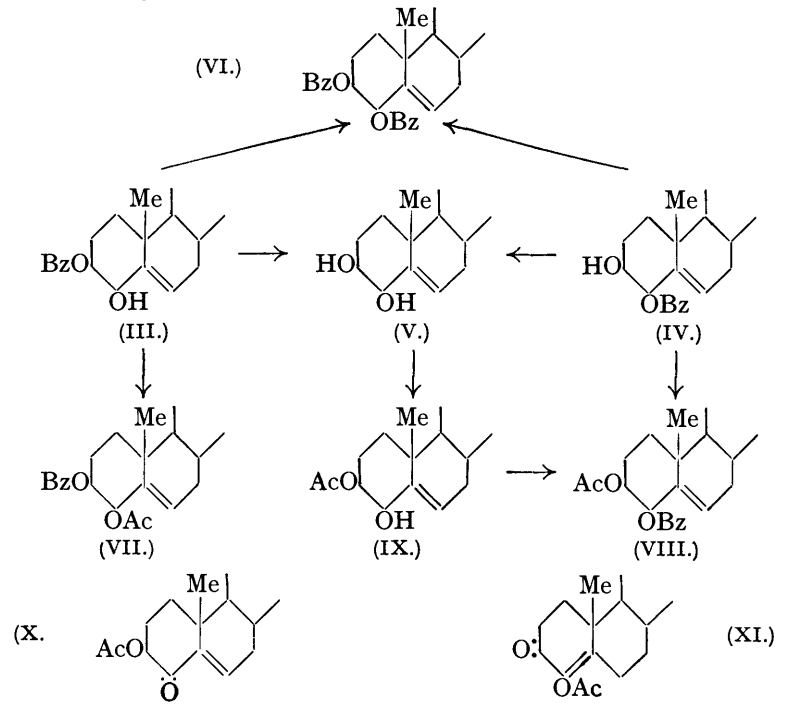
would be obtained; the product proved to be *cis*-3 : 4-dihydroxy-Δ^5-cholestene (V), the identity being established by direct comparison with a specimen prepared by the method of Rosenheim and Starling and also by the preparation of the diacetate, m. p. 168—169°. Benzoylation of compound (C) gave *cis*-3 : 4-dibenzoyloxy-Δ^5-cholestene, m. p. 150—151° (VI). Acetylation, however, gave a *benzoate-acetate*, m. p. 130—131°, differing greatly from the *cis*-3-benzoyloxy-4-acetoxy-Δ^5-cholestene (VII), m. p. 166—167°, described by Rosenheim and Starling. The only feasible explanation of this series of relationships appeared to be that compound (C) is 3-hydroxy-4-benzoyloxy-Δ^5-cholestene (IV), a migration of the benzoyl group from C_3 to C_4 having occurred during its formation; according to this explanation, the benzoate-acetate, m. p. 130—131°, will be 4-benzoyloxy-3-acetoxy-Δ^5-cholestene (VIII). In order to test this explanation, 4-hydroxy-3-acetoxy-Δ^5-cholestene (IX) was prepared by the partial acetylation of the 3 : 4-diol (V) (Petrow and Starling, J., 1940, 60; cf. Marker and Rohrmann, *J. Amer. Chem. Soc.*, 1939, **61**, 3022) and benzoylated; the product, presumably 4-benzoyloxy-3-acetoxy-Δ^5-cholestene (VIII), proved to be identical with the benzoate-acetate, m. p. 130—131°, obtained by acetylation of the compound (C), which accordingly would appear to have the structure (IV).

Reviewing this series of relationships, it is established that two monobenzoates of *cis*-3 : 4-dihydroxy-Δ^5-cholestene exist (m. p.'s 209—210° and 153—154°), which are position isomers and not stereoisomers. The higher-melting isomer has been accorded the 3-benzoate structure (III) on evidence (Rosenheim and Starling, *loc. cit.*) which appears sound: namely, that the 3 : 4-diol (V) gives an insoluble digitonide, whereas the monobenzoate, m. p. 209—210°, fails to do so. We find, however, that the monobenzoate, m. p. 153—154°, likewise fails to give an insoluble digitonide, the conclusions being (*a*) that the presence of a 4-benzoyl group inhibits the formation of an insoluble digitonide in 3-hydroxy-4-benzoyloxy-Δ^5-cholestene, and (*b*) that the position of the ester group in the two monobenzoates of the *cis*-diol is not established. In the same connection we find that the monoacetate of the *cis*-diol described by Petrow and Starling (*loc. cit.*), the esterified hydroxyl group in which must be the same as that in the monobenzoate, m. p. 209—210°, does not give an insoluble digitonide; the second monoacetate of the *cis*-diol is unknown. The reactions of the monoacetate of the *cis*-diol described by Petrow and Starling (*loc. cit.*) have been interpreted by these authors on the then fair assumption that it is the 3-monoacetate (IX). It is noteworthy, however, that an equally valid representation of the reactions is obtained if it is the 4-monoacetate. In particular, reference is made to the intermediate unsaturated keto-acetate, m. p. 124°, obtained by bromination, oxidation, and debromination of the *cis*-diol monoacetate. This compound is formulated as 3-acetoxy-Δ^5-cholesten-4-one (X), a constitution stated to be in conformity with its ultra-violet absorption spectrum, which shows a band at 2800 A. By all analogies the simple $\alpha\beta$-unsaturated ketone (X) would be expected to exhibit an absorption maximum in the region 2300—2500 A. If the monoester is the 4-monoacetate, the intermediate unsaturated keto-acetate must be 4-acetoxy-Δ^4-cholesten-3-one (XI), *i.e.*, a simple diosphenol derivative, a structure which, although in harmony with the formation of cholestane-3 : 4-dione by hydrolysis, is still difficult to reconcile with the light absorption properties, since the mono-enol acetate, m. p. 100—101°, prepared from cholestane-3 : 4-dione by treatment with acetic anhydride exhibits an absorption maximum between 2400 and 2500 A. (Butenandt, *Ber.*, 1936, **69**, 2779) and the mono-enol acetates similarly prepared from forms (A) and (B) of cholestane-2 : 3-dione exhibit absorption maxima at 2380 and 2370 A., respectively (Stiller and Rosenheim, J., 1938, 353). The conversion of the monoacetate of the *cis*-diol into 4-acetoxy-$\Delta^{4:6}$-cholestadien-3-one would be more simply explained if the former is the 4-monoester. However, it must be stressed that evidence of this nature is not conclusive, and for the time being the orientation of the monoesters of *cis*-3 : 4-dihydroxy-Δ^4-cholestene must be considered as not rigidly established.

Analyses of the two products (A) and (B) indicate that they are isomers of the formula $C_{36}H_{54}O_3$ and that each contains an ethoxyl group. This evidence and a consideration of their origin suggest that they are to be formulated as ester-ethers of either *cis*-3 : 4-dihydroxy-Δ^5-cholestene or 3 : 6-dihydroxy-Δ^4-cholestene. In view of the possibility of migration of the benzoyl group there are four probable structures for compounds (A) and

(B). Hydrolysis of compound (A) gives a *diol monoethyl ether*, m. p. 123—124°, $[\alpha]_D$ — 59·2°, characterised by the preparation of the *diol monoethyl ether-acetate*, m. p. 120—121°, $[\alpha]_D$ — 83·5°. Hydrolysis of compound (B) gives a *diol monoethyl ether*, m. p. 122—123° [which differs from the isomer obtained from compound (A)], characterised as its *acetate*, m. p. 150°. A similarity is to be observed in the physical properties of compound (B) and 3-benzoyloxy-6-acetoxy-Δ^4-cholestene (Rosenheim and Starling, *loc. cit.*; Petrow, Rosenheim, and Starling, J., 1938, 677) :

Compound (B)	m. p. 131—132° $[\alpha]_D$ — 29·4°
3-Benzoyloxy-6-acetoxy-Δ^4-cholestene	„ 128—129° „ — 21·2°



This similarity is, moreover, accentuated by the fact that a mixture of the two does not exhibit a melting point depression. This coincidence suggested that compound (B) is 3-benzoyloxy-6-ethoxy-Δ^4-cholestene, formed by direct replacement of the chlorine in (I) by an ethoxyl group. This view, however, is not supported by the fact that the hydrolysis product (diol monoethyl ether) of substance (B) does not give a digitonide. A similar behaviour is observed in the case of the diol monoethyl ether obtained by hydrolysis of substance (A).

Experimental.

Optical rotations were measured in chloroform solution in a 1-dm. tube.

Pyrolysis of β-Cholesteryl Benzoate Oxide.—The oxide (m. p. 151—152°; 10 g.) was heated at 270°/13 mm. for 30 minutes. A sublimate of benzoic acid (1·1 g.) was collected and the residual opaque yellow resin was taken up in hot ethyl acetate (50 c.c.). The crystalline deposit obtained on cooling was recrystallised from ethyl acetate and then from chloroform–ethyl acetate (1 : 1), from which the *compound* (0·2 g.) separated in small yellow needles, m. p. 300—302° (decomp.), $[\alpha]_D^{22°}$ — 16·5° (c = 1·2). The compound is readily soluble in chloroform, sparingly soluble in ethyl acetate, and insoluble in alcohol and light petroleum; it gives an intense cherry-red coloration with antimony trichloride in chloroform [Found : C, 85·1, 84·5; H, 11·2, 11·5; *M*, 1160 (Rast), 1110 (Rieche). $(C_{27}H_{42}O)_3$ requires C, 84·7; H, 11·1%; *M*, 1148].

Concentration of the ethyl acetate mother-liquor gave a crystalline solid (3 g.), m. p. 150—153°, which after three crystallisations from ethyl acetate gave α-cholesteryl benzoate oxide,

m. p. 168—169°, undepressed when mixed with an authentic specimen. Hydrolysis with methyl-alcoholic potassium hydroxide gave α-cholesterol oxide, m. p. 140—141°, undepressed when mixed with an authentic specimen.

Cholestadiene.—A solution of 6-chloro-3-benzoyloxy-Δ^4-cholestene (1 g.) in ether (150 c.c.) was added to aluminium amalgam prepared from aluminium foil (5 g.) as described by Vogel (J., 1927, 594). The mixture was set aside at room temperature for 45 hours, with occasional additions of small amounts of water. The liquid was then filtered and washed with water, and the ether removed from the dried solution. After one crystallisation from ethyl acetate the product (0·8 g.) had m. p. 78—79° and after two further crystallisations from ethyl acetate–methyl alcohol (3 : 1) it gave cholestadiene in long prismatic needles, m. p. 80—81°, $[\alpha]_D^{20°}$ — 129·6° (c = 2·9). It gave an intense orange coloration with tetranitromethane in chloroform and, with antimony trichloride in chloroform, an orange, changing to cherry-red on standing (Found : C, 87·9; H, 12·0. Calc. for $C_{27}H_{44}$: C, 88·0; H, 12·0%).

Treatment of 6-Chloro-3-benzoyloxy-Δ^4*-cholestene with Potassium Acetate in Alcohol. Compound (A).*—6-Chloro-3-benzoyloxy-Δ^4-cholestene (10 g.) was refluxed for 8 hours with freshly fused potassium acetate (40 g.) and absolute alcohol (400 c.c.). The mixture was diluted with water and extracted with ether. The extract was washed with water and dried (sodium sulphate), and the solvent removed. The colourless resin obtained was taken up in hot ethyl acetate (20 c.c.) and methyl alcohol (7 c.c.). The crystalline solid separating on standing (1·1 g.; m. p. 145—155°) was twice crystallised from ethyl acetate–methyl alcohol (4 : 1), from which the *diol monoethyl ether benzoate* (compound A) separated in plates, m. p. 166—167° (const.), $[\alpha]_D^{20°}$ — 47·2° (c = 0·85). It was readily soluble in chloroform and hot ethyl acetate but sparingly soluble in alcohol and gave an intense violet coloration with antimony trichloride in chloroform. A mixture with 3-benzoyloxy-4-acetoxy-Δ^5-cholestene, m. p. 166—167° (for which we are indebted to Dr. O. Rosenheim), melted at 155—157° (Found : C, 80·6; H, 10·3; OEt, 8·5. $C_{36}H_{54}O_3$ requires C, 80·85; H, 10·2; OEt, 8·4%).

Diol Monoethyl Ether.—Compound (A) (0·2 g.) was refluxed for 3 hours with methyl-alcoholic potassium hydroxide (20 c.c.; 3%). The crystalline solid separating on cooling was recrystallised from methyl alcohol, yielding the *diol monoethyl ether* in blades, m. p. 123—124°, $[\alpha]_D^{20°}$ — 59·2° (c = 0·76). With the antimony trichloride reagent a pink colour developed after about 1 minute; the diol ether gave a weak yellow coloration with tetranitromethane in chloroform (Found : C, 80·5; H, 11·4; OEt, 11·3. $C_{29}H_{50}O_2$ requires C, 80·9; H, 11·7; OEt 10·5%).

Diol Monoethyl Ether Acetate.—The diol monoethyl ether (0·3 g.) was refluxed for 1 hour with acetic anhydride (2 c.c.) and pyridine (2 c.c.). The product, isolated by the addition of water, was crystallised from ethyl acetate–methyl alcohol (1 : 2), from which the *diol monoethyl ether acetate* separated in plates, m. p. 120—121°, $[\alpha]_D^{20°}$ — 83·5° (c = 2·1). It gave an intense red-violet coloration with the antimony trichloride reagent (Found : C, 78·4; H, 11·4. $C_{31}H_{52}O_3$ requires C, 78·8; H, 11·1%).

Compound (B).—Concentration of the original ethyl acetate–methyl alcohol mother-liquor obtained after removal of the crude compound (A) (m. p. 144—155°) gave a crystalline solid (4·8 g.). This was fractionally crystallised from ethyl acetate–methyl alcohol. The top crop was repeatedly crystallised from the same solvent mixture, giving the *diol monoethyl ether benzoate* (compound B) (0·8 g.) in needles, m. p. 131—132°, $[\alpha]_D^{20°}$ — 29·4° (c = 1·2). It was readily soluble in chloroform, less so in ethyl acetate, and sparingly soluble in alcohol. With the antimony trichloride reagent it gave a violet solution. The m. p. of compound (B) is not depressed when this is mixed with 3-benzoyloxy-6-acetoxy-Δ^4-cholestene (m. p. 128—129°) (kindly supplied by Dr. O. Rosenheim) (Found : C, 80·8; H, 10·1; OEt, 8·1. $C_{36}H_{54}O_3$ requires C, 80·85; H, 10·2; OEt, 8·4%).

Diol Monoethyl Ether.—The above benzoate (0·5 g.) was refluxed for 1½ hours with methyl-alcoholic potassium hydroxide (40 c.c.; 2½%). The product was isolated by the addition of water, washed, and crystallised from methyl alcohol, from which the *diol monoethyl ether* separated in needles, m. p. 107—108°. After drying in a vacuum over phosphoric oxide at 78° for 6 hours, the compound melted sharply at 122—123°. A mixture with the diol monoethyl ether (m. p. 123—124°) obtained by hydrolysis of compound (A) melted at 100°. With the antimony trichloride reagent the new diol ether gave a violet coloration and with tetranitromethane in chloroform a pale yellow solution (Found : C, 80·6; H, 11·6; OEt, 10·6. $C_{29}H_{50}O_2$ requires C, 80·9; H, 11·7; OEt, 10·5%).

The diol monoethyl ether (0·2 g.) was refluxed for 1 hour with pyridine (1·5 c.c.) and acetic anhydride (1·5 c.c.). The crystalline solid separating on cooling was recrystallised from ethyl acetate–methyl alcohol (1 : 1), from which the *diol monoethyl ether acetate* separated in prismatic

needles, m. p. 150°. It gave a violet coloration with the antimony trichloride reagent (Found : C, 78·3; H, 11·05. $C_{31}H_{52}O_3$ requires C, 78·8; H, 11·1%).

Monobenzoate of cis-3 : 4-*Dihydroxy*-Δ^5-*cholestene* (*Compound C*).—Concentration of the ethyl acetate–methyl alcohol mother-liquor obtained after removal of the top crop (above), followed by repeated crystallisation of the product from the same solvent mixture (2 : 3), gave the *monobenzoate* of the *cis*-diol (1·5 g.) in leaflets, m. p. 153—154°, $[\alpha]_D^{20°}$ − 27·8° (*c* = 1·8). This gave a pink coloration with the antimony trichloride reagent and a yellow coloration with tetranitromethane in chloroform (Found : C, 80·8; H, 10·0. $C_{34}H_{50}O_3$ requires C, 80·6; H, 9·9%). When it was treated in warm alcoholic solution with a solution of digitonin (1% in 90% alcohol), no separation of a digitonide occurred. Under the same (standard) conditions, cholesterol and *cis*-3 : 4-dihydroxy-Δ^5-cholestene gave immediate precipitates of the corresponding digitonides.

The diol monobenzoate (0·5 g.) was refluxed for 1½ hours with methyl-alcoholic potassium hydroxide (3%; 20 c.c.). The product was crystallised from methyl alcohol, giving *cis*-3 : 4-dihydroxy-Δ^5-cholestene in blades, m. p. 175°, $[\alpha]_D^{20°}$ − 61·5° (*c* = 1·7); the m. p. was not depressed by the 3 : 4-diol, m. p. 175—176°, prepared by hydrolysis of 4-hydroxy-3-benzoyloxy-Δ^5-cholestene, m. p. 209—210° (prepared as described by Rosenheim and Starling, *loc. cit.*). Rosenheim and Starling give m. p. 176—177°, $[\alpha]_D$ − 60·0° for the *cis*-3 : 4-diol. Acetylation of the *cis*-3 : 4-diol, m. p. 175°, gave *cis*-3 : 4-diacetoxy-Δ^5-cholestene in needles, m. p. 168—169°, $[\alpha]_D^{20°}$ − 97·4° (*c* = 1·3) (Found : C, 76·6; H, 10·35. Calc. for $C_{31}H_{50}O_4$: C, 76·5; H, 10·4%); the m. p. was not depressed by the diacetate, m. p. 168—169°, obtained from the diol, m. p. 175—176°. Rosenheim and Starling give m. p. 169—170°, $[\alpha]_D$ − 96·1° for the *cis*-3 : 4-diacetate.

cis-3 : 4-*Dibenzoyloxy*-Δ^5-*cholestene*.—The monobenzoate, m. p. 153—154° (0·5 g.), was heated on the steam-bath for 30 minutes with pyridine (5 c.c.) and benzoyl chloride (5 c.c.). The mixture was diluted with sodium carbonate solution (10%) and extracted with ether. The product was crystallised from ethyl acetate–methyl alcohol (1 : 1), from which the dibenzoate separated in needles, m. p. 150—151°, not depressed by a specimen prepared by the method of Rosenheim and Starling (*loc. cit.*) but depressed to 130° by the monobenzoate, m. p. 153—154°.

Benzoate-acetate of cis-3 : 4-*Dihydroxy*-Δ^5-*cholestene*.—(a) The monobenzoate of the *cis*-diol (m. p. 153—154°; 0·3 g.) was refluxed for 1½ hours with pyridine (2 c.c.) and acetic anhydride (2 c.c.). Water was added to the cooled solution, and the crystalline deposit recrystallised from ethyl acetate–methyl alcohol (1 : 1), from which the benzoate-acetate separated in fine needles, m. p. 130—131° (const.), $[\alpha]_D^{20°}$ − 54·8° (*c* = 1·2). It gave an intense violet coloration with antimony trichloride in chloroform (Found : C, 78·5; H, 9·8. $C_{36}H_{52}O_4$ requires C, 78·7; H, 9·6%). Hydrolysis of this compound by the method described for the parent diol monobenzoate gave *cis*-3 : 4-dihydroxy-Δ^5-cholestene, m. p. 175° either alone or when mixed with an authentic specimen, m. p. 175—176°.

(b) The monoacetate of the *cis*-diol (Petrow and Starling, *loc. cit.*) (0·3 g.) was heated on the steam-bath for 1 hour with benzoyl chloride (3 c.c.) and pyridine (3 c.c.). The product, isolated in the usual manner, was twice crystallised from methanol, from which the benzoate-acetate separated in fine needles, m. p. 129—130°, $[\alpha]_D^{20°}$ − 54·4° (*c* = 1·7), not depressed by the specimen prepared by method (a).

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