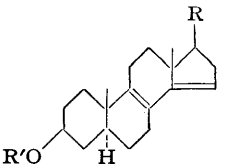
51. *The Application of the Method of Molecular Rotation Differences to Steroids. Part VII. Olefinic Unsaturation at the* 8(9)-*Position.*

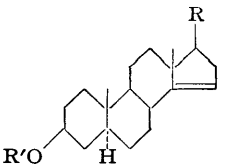
By D. H. R. Barton and J. D. Cox.

Under suitable conditions the catalytic hydrogenation of dehydro-α-ergostenyl acetate affords a mixture of ergost-8(14)-en-3(β)-yl acetate and *ergost*-8(9)-*en*-3(β)-*yl acetate*. The molecular rotation differences between the latter and its derivatives and between zymostenyl acetate and its corresponding derivatives are identical, thus indicating an identical position for the ethylenic linkage. This has been confirmed by catalytic hydrogenation of *iso*dehydrocholesteryl acetate which, contrary to previous views, furnishes a mixture of cholest-7(8)-en-3(β)-yl acetate and cholest-8(9)-en-3(β)-yl acetate, the latter having properties in agreement with those recorded for zymostenyl acetate. Zymosterol and related yeast-fat sterols must, therefore, possess an 8(9)-ethylenic linkage instead of one at 8(14) or 9(11) as previously suggested by other workers.

In Part II of this series (*J.*, 1946, 512) the formula (I; R = C_9H_{19}, R′ = H) was assigned to dehydro-α-ergostenol in agreement with the views of previous workers. It would be expected from analogy with the ease of catalytic hydrogenation of β-ergostenol (II; R = C_9H_{19}, R′ = H), that dehydro-α-ergostenol would be similarly reduced to the hitherto unknown ergost-8(9)-en-3(β)-ol (III; R = C_9H_{19}, R′ = H). However this is not the case and dehydro-α-ergostenyl acetate was recovered unchanged after being subjected to a variety of mild reduction procedures which are normally applicable to conjugated dienes (cf. Bernstein and Dorfman, *J. Amer. Chem. Soc.*, 1946, **68**, 1663). It was finally discovered that high-pressure hydrogenation of dehydro-α-ergostenyl acetate at 100° in alcoholic solution using Raney nickel as catalyst gave a mixture of α-ergostenyl acetate (IV; R = C_9H_{19}, R′ = Ac) and the required *ergost*-8(9)-*en*-3(β)-*yl acetate* (III; R = C_9H_{19}, R′ = Ac). We are of the opinion that in this reaction both 1:2- and 1:4-addition of hydrogen occurs rather than that the α-ergostenyl acetate is formed by

rearrangement of (III; R = C_9H_{19}, R′ = Ac). This view is supported by the fact that roughly the same ratio of the two products was obtained whether the hydrogenation was carried out for


(I.)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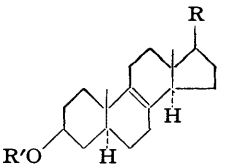
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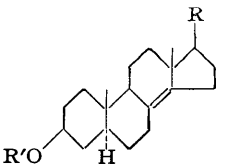

(IV.)

three hours or overnight. Nevertheless, as would be expected, ergost-8(9)-en-3(β)-yl acetate was quantitatively rearranged to α-ergostenyl acetate on shaking with a platinum catalyst in ether–acetic acid solution in the presence of hydrogen.

TABLE I.

Substance.	$[M]_D$, Alcohol.	Acetate.	Benzoate.	Δ_1.	Δ_2.	Refs.
Ergost-7(8)-en-3(β)-ol	− 8°	− 18°	+ 10°	−10°	+18°	1
Ergost-8(14)-en-3(β)-ol	+ 44	+ 4	± 0	−40	−44	1
Ergost-8(9)-en-3(β)-ol	+156	+110	+171	−46	+15	2
Zymostenol	+193	+146	+201	−47	+ 8	2, 3

1. Part IV; *J.*, 1948, 783. 2. Exptl. 3. Part I, *J.*, 1945, 813.

TABLE II.

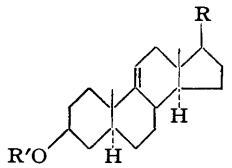
Substance.	$[M]_D$, Unsaturated.	Saturated.	Δ.	Refs.
Ergost-8(9)-en-3(β)-ol	+156°	+60°	− 96°	2, 4
Zymostenol	+193	+89	−104	3, 5
Ergost-8(9)-en-3(β)-yl acetate	+110	+27	− 83	2, 4
Zymostenyl acetate	+146	+60	− 86	2, 3, 5
Ergost-8(9)-en-3(β)-yl benzoate	+171	+66	−105	2, 4
Zymostenyl benzoate	+201	+94	−107	3, 5

4. Part V, *J.*, 1948, 1354. 5. Part III, *J.*, 1946, 1116.

The molecular rotation differences for ergost-8(9)-en-3(β)-ol on acylation and especially with respect to ergostan-3(β)-ol are highly characteristic and quite different from those recorded for comparable isomeric ergostenols (see Tables I and II). It was especially interesting, however, that these Δ values were identical, within the limits of experimental error, with those recorded in the literature for zymostenol, the dihydro-derivative of zymosterol (see Tables I and II). Zymosterol, itself, has been the subject of a number of investigations particularly that of Heath-Brown, Heilbron, and Jones (*J.*, 1940, 1482). The latter workers proved the identity of the saturated zymostanol with cholestan-3(β)-ol and also the position of the side chain ethylenic linkage at 24(25). They finally concluded that zymosterol was cholesta-8(14) : 24(25)-dien-3(β)-ol (IV; R = C_8H_{15}, R′ = H). Later Wieland, Rath, and Benend (*Annalen*, 1941, **548**, 19) found that on catalytic hydrogenation in neutral solution zymosteryl benzoate afforded the monoethenoid zymostenyl benzoate, the hydrolysis product of which was not identical with any known cholestenol. Since, in particular, zymostenol was not identical with either the δ-cholestenol of Windaus, Linsert, and Eckhardt (*ibid.*, 1938, **534**, 22) to which the formula (III; R = C_8H_{17}, R′ = H) had been given, or with α-cholestenol (IV; R = C_8H_{17}, R′ = H), it was assigned the formula (V; R = C_8H_{17}, R′ = H). This latter formula was thought to explain the formation of α-cholestenol from zymosterol on hydrogenation in acidic solution.

It will be recalled that δ-cholestenol [acetate, m. p. 107—108°, $[\alpha]_D$ +14° (in chloroform)] was first obtained by Windaus, Linsert, and Eckhardt (*loc. cit.*) by the sodium–*iso*propyl alcohol reduction of *iso*dehydrocholesterol (VI; R = C_8H_{17}, R′ = H). At the same time a smaller quantity of ε-cholestenol [acetate, m. p. 118°, $[\alpha]_D$ +21° (in chloroform), more readily eluted from alumina than the acetate of the δ-isomer] was said to be formed. The homogeneity of δ-cholestenol received apparent confirmation from the experiments of Wieland and Benend (*Annalen*, 1943, **554**, 1) who claimed that catalytic hydrogenation of *iso*dehydrocholesteryl

acetate (VI; R = C_8H_{17}, R′ = Ac) in neutral solution afforded, in almost quantitative yield, pure δ-cholestenyl acetate. In Part I of this series (*J.*, 1945, 813) it was pointed out that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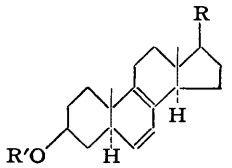
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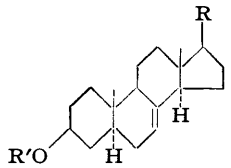
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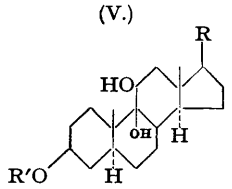
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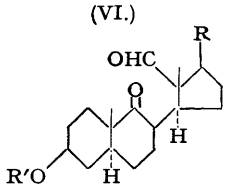
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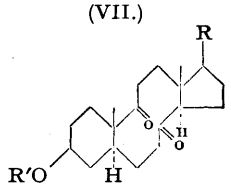
(X.)

δ-cholestenol possessed an anomalous positive Δ_1 value and that this anomaly needed confirmation. Through the courtesy of Professor Windaus (Göttingen), to whom we wish to express our deep appreciation, we have been enabled to undertake a further investigation of the catalytic hydrogenation of *iso*dehydrocholesterol derivatives. Contrary to the views of Wieland and Benend we had no difficulty in showing, by the chromatographic method, that the product of catalytic hydrogenation of *iso*dehydrocholesteryl acetate is not homogeneous. From the more difficultly eluted fractions it was possible to isolate, as the benzoate, γ-cholestenol (VII; R = C_8H_{17}, R′ = H), whilst from the more easily eluted fractions an acetate was obtained with properties in satisfactory agreement with those recorded for zymostenyl acetate and to which we give the formula (III; R = C_8H_{17}, R′ = Ac). Catalytic hydrogenation of *iso*dehydrocholesteryl acetate proceeds, therefore, by both 1 : 2 and 1 : 4 addition of hydrogen as in the case of dehydro-α-ergostenyl acetate (see above).

Catalytic hydrogenation of *iso*dehydrocholesteryl benzoate in neutral solution led, as with the acetate, to the rapid uptake of only one molecular proportion of hydrogen. The product, on crystallisation, appeared to be homogeneous and corresponded in properties to a molecular complex of equal parts of γ-cholestenyl benzoate (VII; R = C_8H_{17}, R′ = Bz) and cholest-8(9)-en-3(β)-yl benzoate (III; R = C_8H_{17}, R′ = Bz).

These experiments lead us to conclude that zymosterol is cholesta-8(9) : 24(25)-dien-3(β)-ol (III; R = C_8H_{15}, R′ = H) and that ascosterol and faecosterol, whose nuclear double bonds we have previously demonstrated to occupy the same position as that in zymosterol (see Part I, *J.*, 1945, 813), have analogous formulæ. They also provide final confirmation of the absence of 8(9)-unsaturation in α-dihydroergosterol and α-spinasterol (see Part V; *ibid.*, 1948, 1354).

In support of the formula (V; R = C_8H_{17}, R′ = H) for zymostenol, Wieland and Benend (*Ber.*, 1942, **75**, 1708) treated the benzoate with osmium tetroxide and, after hydrolysis of the product, isolated a cholestanetriol which they regarded as (VIII; R = C_8H_{17}, R′ = H). In agreement with this formula a diacetate was prepared under mild conditions and the triol itself was split by lead tetra-acetate to a substance formulated as the keto-aldehyde (IX; R = C_8H_{17}, R′ = H). No proof was offered for the presence of the aldehyde group in the latter compound and it is now to be formulated as the diketone (X; R = C_8H_{17}, R′ = H). The formation of a diacetate from the cholestanetriol does not, however, receive a convincing explanation on the basis of our experiments.*

Added. July 9th. It should be pointed out that steroids which are known to have an olefinic linkage at the 9(11)-position, like androst-9(11)-en-3(β)-ol (Shoppee, *Helv. Chim. Acta*, 1940, **23**, 740; Reich and Lardon, *ibid.*, 1947, **30**, 329; Shoppee, *J.*, 1946, 1134; *Helv. Chim. Acta*, 1947, **30**, 766), androst-9(11)-en-3(α)-ol (Mason and Kepler, *J. Biol. Chem.*, 1945, **161**, 235) and a number of 9(11)-unsaturated bile acids (cf. Seebeck and Reichstein, *Helv. Chim. Acta*, 1943, **26**, 536; Reich and Reichstein, *ibid.*, p. 562; Lardon and Reichstein, *ibid.*, 1945, **28**, 1420) are all readily hydrogenated in acetic acid solution using a platinum catalyst. This is in

* Professor L. F. Fieser (Harvard) has drawn our attention to the fact that the calculated figures for Wieland and Benend's supposed diacetate should be: C, 73·76; H, 10·39; and not as stated by them (see also Fieser and Fieser, "Natural Products Related to Phenanthrene," 3rd edit.).

marked contrast to substances like zymosterol and other yeast fat sterols which really have 8(9)-olefinic linkages (see earlier).

Experimental.

(M. p.s are uncorrected.)

The substances whose rotations are listed below were dried in a vacuum, before weighing, at 20° below their m. p.s, or at 120°, whichever was the lower temperature. All rotations are for the Na_D line and in chloroform solution. They were taken in 1 dm. macro- or micro-tubes, the use of the latter being specifically indicated after each recorded measurement.

Standard chemical operations were carried out as in Part IV (*J.*, 1948, 783) unless specified to the contrary.

Micro-analyses are by Drs. Weiler and Strauss, Oxford.

Dehydro-α-ergostenyl Acetate.—The method of preparation using selenium dioxide (see Part IV; *loc. cit.*) is not very convenient for obtaining material to use in hydrogenation experiments because of the repeated chromatography needed for removal of the last traces of selenium. The following procedure, using performic acid, furnishes a higher yield and, at the same time, overcomes this difficulty.

8·6 G. of α-ergostenyl acetate were dissolved in 50 ml. of chloroform and mixed with 10 ml. of 30% hydrogen peroxide and 10 ml. of anhydrous formic acid. The mixture (two phases) was left to stand at room temperature for 7 days. The chloroform layer was separated, washed free of acid, and the chloroform removed under reduced pressure. The product was taken up in 50 ml. of absolute alcohol containing a few drops of concentrated sulphuric acid and refluxed on the water-bath for 30 minutes. The acid was neutralised, water and ether added, and the ethereal layer separated. After removal of the ether the residue was acetylated in the usual way to give, after several recrystallisations from chloroform–methanol, 1·7 g. (20% of theory) of dehydro-α-ergostenyl acetate, m. p. 135°.

Comparative Experiments on the Hydrogenation of β-Ergostenol.—β-Ergostenol on hydrogenation either in dry ether or in acetic acid–ether using a platinum oxide catalyst gave, in almost quantitative yield, pure ergostanol, m. p. 141·5°, $[\alpha]_D$ +15° (*c*, 1·82). The product from the neutral hydrogenation showed no colour with the Liebermann–Burchard reagent; that from the acid hydrogenation gave a very faint colour. Our previous experience with mixtures of α-ergostenol and ergostanol indicates that only traces of the former can have been present in these hydrogenation products.

Attempted Reduction of Dehydro-α-ergostenyl Acetate.—Dehydro-α-ergostenyl acetate was recovered unchanged after attempted hydrogenation in both ethereal and ethyl acetate solutions using a platinum catalyst and one atmosphere hydrogen pressure. Dehydro-α-ergostenol was recovered unchanged after attempted reduction of the acetate with dissolving sodium in boiling ethyl, *iso*propyl, and *n*-butyl alcohols.

High-pressure Hydrogenation of Dehydro-α-ergostenyl Acetate.—Dehydro-α-ergostenyl acetate was recovered unchanged after stirring in anhydrous ether solution with platinum oxide catalyst at room temperature and 100 atm. hydrogen pressure. Reduction was effected, however, when a solution of 1·4 g. of dehydro-α-ergostenyl acetate in 60 ml. of absolute ethyl alcohol, was stirred overnight with 3 g. of freshly prepared Raney nickel at 100° and 100 atmospheres hydrogen pressure. Catalyst and solvent were removed to give a product, which had, when crystallised from ethyl acetate–methanol, m. p. 149—152°, $[\alpha]_D$ +20° (*c*, 3·07). On recrystallisation to constant m. p. and rotation *ergost*-8(9)-*en*-3(β)-*yl acetate*, m. p. 157—158·5°, $[\alpha]_D$ +24° (*c*, 2·18), +25° (*c*, 2·16; micro-tube), $[M]_D$ +110°, was obtained (Found: C, 81·1; H, 11·1. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·3%). There was no absorption in the ultra-violet. Alkaline hydrolysis of this acetate furnished *ergost*-8(9)-*en*-3(β)-*ol*, recrystallised from chloroform–methanol; m. p. 153—155°, $[\alpha]_D$ +39° (*c*, 2·75; micro-tube), +39° (*c*, 2·16; micro-tube), $[M]_D$ +156° (Found: C, 80·2; H, 11·8. $C_{28}H_{48}O,H_2O$ requires C, 80·4; H, 12·0%). The alcohol readily furnished a digitonide. By treatment with benzoyl chloride in pyridine solution at room temperature this alcohol afforded *ergost*-8(9)-*en*-3(β)-*yl benzoate*, recrystallised from chloroform–ethanol; m. p. 147—148°, $[\alpha]_D$ +34° (*c*, 1·70; micro-tube) (Found: C, 82·8; H, 10·2. $C_{35}H_{52}O_2$ requires C, 83·3; H, 10·3%). On treatment of 50 mg. of ergost-8(9)-en-3(β)-yl benzoate in chloroform with a slight excess of perbenzoic acid solution in the same solvent and leaving to stand for 4 days at 0°, 1·06 molecular proportions of perbenzoic acid were consumed.

The mother liquors from the crystallisation of ergost-8(9)-en-3(β)-yl acetate were evaporated under reduced pressure and the residue hydrolysed and benzoylated. The resulting benzoate was crystallised from ethyl acetate–ethanol to give the following fractions (in order of increasing solubility):—(i) Large plates, m. p. 129—132°, $[\alpha]_D$ +18° (*c*, 1·78). (ii) A mixture of plates and needles, m. p. *ca.* 120° unsharply. (iii) Rosettes of needles, m. p. 116°, unchanged on several recrystallisations from ethyl acetate–methanol, $[\alpha]_D$ ±0° (*c*, 2·15). This substance was identified as α-ergostenyl benzoate and gave no depression in m. p. with an authentic specimen, m. p. 116°, $[\alpha]_D$ ±0° (see Part IV; *loc. cit.*).

Reactions of the 8(9) *Double Bond.*—Ergost-8(9)-en-3(β)-ol and its derivatives gave the same colours as ergost-8(14)-en-3(β)-ol and ergost-7(8)-en-3(β)-ol and their derivatives in the Tortelli–Jaffé and the Liebermann–Burchard reaction. There was a marked contrast in behaviour, however, with osmium tetroxide in anhydrous ether solution. Both zymosteryl acetate (for a specimen of which we are much indebted to Professor E. R. H. Jones) and ergost-8(9)-en-3(β)-ol gave heavy precipitates a few minutes after mixing. Ergost-14(15)-en-3(β)-ol behaved similarly, but ergost-8(14)-en-3(β)-ol and ergost-7(8)-en-3(β)-ol only afforded precipitates after standing for several days.

Rearrangement of Ergost-8(9)-*en*-3(β)-*yl Acetate to α-Ergostenyl Acetate.*—35 Mg. of ergost-8(9)-en-3(β)-yl acetate, dissolved in 20 ml. of 1 : 1 ether–acetic acid solution, were shaken with 50 mg. of platinum catalyst in an atmosphere of hydrogen for 10 hours. After recrystallisation of the product from ethyl acetate–methanol 25 mg. of pure α-ergostenyl acetate, m. p. 108·5°, $[\alpha]_D$ +1° (*c*, 1·00; micro-tube), undepressed in m. p. on admixture with an authentic specimen, were isolated.

iso*Dehydrocholesteryl* p-*Nitrobenzoate.*—As supplied by Professor A. Windaus this substance had

m. p. 162° (decomp.) $[\alpha]_D$ −3·5° (*c*, 8·51). Recrystallised twice from chloroform–ethyl acetate gave m. p. 165° (decomp.), $[\alpha]_D$ −3° (*c*, 7·18).

iso*Dehydrocholesterol.*—Prepared by alkaline hydrolysis of the *p*-nitrobenzoate, *iso*dehydrocholesterol, recrystallised from ethyl acetate–methanol, had m. p. 115—116°, $[\alpha]_D$ −10° (*c*, 2·24).

iso*Dehydrocholesteryl Acetate.*—This compound was obtained by refluxing *iso*dehydrocholesterol with acetic anhydride. Recrystallised from chloroform–methanol it had m. p. 109° (to a cloudy melt, clearing at 117—118°), $[\alpha]_D$ −5° (*c*, 3·13), −6° (*c*, 1·58).

iso*Dehydrocholesteryl Benzoate.*—This substance, recrystallised from ethyl acetate–methanol, had m. p. 143—144°, $[\alpha]_D$ −3° (*c*, 3·85).

All these derivatives of *iso*dehydrocholesterol melt somewhat lower than found by Windaus, Linsert, and Eckhardt (*Annalen*, 1938, **534**, 22) and also have rotations which are more positive. The German authors noted that *iso*dehydrocholesterol was liable to contamination with an unsaturated substance having $\lambda_{max.}$ at 240 mμ and possessing a weakly positive rotation. This substance cannot be responsible, however, for the small discrepancy between our results and the previous observations because our purified *iso*dehydrocholesteryl acetate had, in alcoholic solution, $\lambda_{max.}$ at 271 and 278 mμ, both with $\epsilon = 3800$, and gave no indication of a maximum at 240 mμ.

Hydrogenation of iso*Dehydrocholesteryl Acetate.*—2·0 G. of *iso*dehydrocholesteryl acetate dissolved in 80 ml. of ethyl acetate were hydrogenated using 250 mg. of platinum oxide catalyst. After ¾ hour the hydrogen absorption ceased, at which time the theory for one double bond had been taken up. After removal of the catalyst by filtration and the solvent by evaporation under reduced pressure the residue had m. p. 105°, unchanged by recrystallisation from ethyl acetate, $[\alpha]_D$ +21° (*c*, 2·79).

This product was chromatographed over Birlec alumina and gave the following chromatogram, each fraction of which corresponds to 80 ml. of eluate unless specified to the contrary.

Fraction.	Eluent.	M. p. after recrystn. from ethyl acetate–methanol.
1	500 Ml. light petroleum (40—60°)	Trace of oil
2	95 : 5 Light petroleum : benzene	*ca.* 110°
3	,,	*ca.* 110
4	,,	105—108
5	,,	104—106
6	,,	103—105
7	,,	99—101
8	,,	104—105
9	,,	105—106
10	,,	105—106
11	,,	106—107
12	,,	106—107
13	Chloroform	107—108
14	250 Ml. 90 : 10 chloroform : methanol	Negligible

On repeated crystallisation from ethyl acetate–methanol the m. p. of fraction 2 finally rose to 125—126°, $[\alpha]_D$ +35° (*c*, 1·08; micro-tube). For zymostenyl acetate Wieland, Rath, and Benend (*Annalen*, 1941, **548**, 19) give m. p. 128—129°, $[\alpha]_D$ +32°. Alkaline hydrolysis of this acetate gave an alcohol, recrystallised from methanol; m. p. 129°, $[\alpha]_D$ +50° (*c*, 0·14; micro-tube); this on benzoylation gave a benzoate, recrystallised from methanol; m. p. 139—140°. For zymostenol and zymostenyl benzoate Wieland, Rath, and Benend (*loc. cit.*) give m. p. 128—129°, $[\alpha]_D$ +50° and m. p. 140—142° respectively.

Fractions 3 to 7 were combined, added to the solids from the mother liquors from crystallisation of all the chromatogram fractions and the whole recrystallised from ethyl acetate–methanol; m. p. 105—106°, $[\alpha]_D$ +22° (*c*, 2·70). Further chromatography gave about eleven fractions the first three of which were combined and recrystallised from ethyl acetate–methanol; m. p. 109—111°, $[\alpha]_D$ +27° (*c*, 1·81; micro-tube). Similar rechromatography of this material afforded, in the same way, three top fractions which, when combined, had m. p. 117—119°, $[\alpha]_D$ +27° (*c*, 2·59; micro-tube). Clearly it was not possible to obtain a further quantity of cholest-8(9)-en-3(β)-yl acetate by this method, which is an indication that a further component besides cholest-7(8)-en-3(β)-yl acetate (presumably cholest-8(14)-en-3(β)-yl acetate) was probably present.

Fraction 13 of the first chromatogram, which had m. p. 107—108° (see above) and $[\alpha]_D$ +8° (*c*, 3·10), confirmed that the less dextrorotatory component was concentrated in the more difficultly eluted fractions. Fractions 8 to 13 were combined and recrystallised from ethyl acetate–methanol; m. p. 106—107°, $[\alpha]_D$ +15° (*c*, 2·46). On alkaline hydrolysis an alcohol mixture, m. p. 120—121°, $[\alpha]_D$ +18° (*c*, 2·11), was obtained after crystallisation from ethyl acetate–methanol. These rotations correspond to a Δ_1 value of −5° from which it must be concluded that some concentration of cholest-7(8)-en-3(β)-ol occurs on crystallisation. The alcohol mixture, m. p. 120—121°, was benzoylated in the usual way and the benzoate recrystallised many times from ethyl acetate. The m. p. finally became constant at 155—156°, $[\alpha]_D$ +9° (*c*, 0·74; micro-tube). For cholest-7(8)-en-3(β)-yl benzoate, Schenck, Buchholz, and Wiese (*Ber.*, 1936, **69**, 2696) record m. p. 157—158°, $[\alpha]_D$ +7°. The specimen of cholest-7(8)-en-3(β)-yl benzoate thus prepared was hydrolysed in the usual way to give cholest-7(8)-en-3(β)-ol, m. p. 122—123°, from which the acetate, m. p. 117—118°, was prepared. For cholest-7(8)-en-3(β)-ol and its acetate Schenck, Buchholz, and Wiese (*loc. cit.*) give m. p.s 122—123° and 118—119° respectively.

A hydrogenation comparable to that recorded above, using chloroform as solvent, similarly led to the rapid absorption of one molecular proportion of hydrogen. After working up, the product had m. p. 92—93°, $[\alpha]_D$ +12° (*c*, 1·01), and on hydrolysis gave an alcohol mixture, m. p. 115—116°, $[\alpha]_D$ +21° (*c*, 1·61). In this experiment partial rearrangement to cholest-8(14)-en-3(β)-yl acetate must have occurred as is shown by the low m. p. and rotation.

Hydrogenation of iso*Dehydrocholesteryl Benzoate.*—1·60 G. of *iso*dehydrocholesteryl benzoate dissolved in 100 ml. of ethyl acetate were hydrogenated using 200 mg. of platinum oxide catalyst. After ½ hour the hydrogen absorption ceased, at which time the theory for one double bond had been taken up. After working up in the usual way an apparently homogeneous product, m. p. 142—143°, $[\alpha]_D$ +23° (*c*, 4·43), +23° (*c*, 2·21), was obtained whose constants were not changed on repeated recrystallisation. It was probably a 1 : 1 molecular complex of cholest-7(8)-en-3(β)-yl benzoate and cholest-8(9)-en-3(β)-yl benzoate for which the calculated rotation is +24°, and accordingly was not investigated further.

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