Anal. Calcd. for $C_8H_{12}SO_5$: C, 43.63; H, 5.49. Found: C, 43.64; H, 5.48.

Oxidation of XVII with aqueous potassium permanganate or with nitric acid gave β,β-dimethylglutaric acid, m. p. 98–99° (variously reported,[38] 100° to 104°); neutral equivalent: calcd., 80.1; found, 79.2. The β,β-dimethylglutaric acid was identified further by conversion to the anil, **N-phenyl-β,β-dimethylglutarimide**, of m. p. 156–157°; reported,[39] 157°.

S-Benzylthiuronium 5,5-dimethyldihydroresorcinol-2-sulfonate, at first quite soluble in methanol, changed on scratching to a much less soluble form, m. p. 157.5–158.5°.

Anal. Calcd. for $C_{16}H_{22}N_2S_2O_5$: C, 49.72; H, 5.74. Found: C, 49.41; H, 5.90.

The **pyridinium 5,5-dimethyldihydroresorcinol-2-sulfonate**, formed in good yield from the components in acetonitrile, crystallizes as large colorless prisms, m. p. 141–141.5°.

4,5-Dimethylresorcinol (XVIII).—A solution of 44.0 g. of XVII in 100 cc. of acetic anhydride was refluxed for four hours, the initial evolution of sulfur dioxide being copious, and then evaporated to dryness *in vacuo*. The residue was refluxed two hours with aqueous (200 cc.) sodium hydroxide (80 g.). An ethereal extract of the cooled, acidified solution was concentrated to a residue, crystallization of which from benzene gave 6.70 g. (2.13 g. from second crop) of orange crystals. Sublimation and recrystallization from benzene gave pure colorless XVIII, m. p. 135.5–136° (reported,[40] m. p. 133–134.5° and 134–135°).

Anal. Calcd. for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.45; H, 7.30.

The reaction of XVIII with benzoyl chloride in the presence of sodium carbonate gave the sodium hydroxide-soluble, heptane-crystallizable ***o*-xylorcinol monobenzoate**, m. p. 121–121.5°.

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.55; H, 5.71.

When, instead of sodium carbonate, 2 *N* sodium hydroxide (15 cc. at first and 15 cc. more in three portions) and benzoyl chloride (2.32 cc. at first and then 2.32 cc. in three portions) reacted with XVIII (1.38 g.), an ethereal extract was obtained which after washing with alkali and water and evaporating yielded a crude neutral oil. On crystallization from 5 cc. of ethanol, 3.18 g. (92%) of ***o*-xylorcinol dibenzoate** was obtained. Recrystallization from ethanol, sublimation, and recrystallization gave pure material, m. p. 102–103° (reported,[41] m. p. 100–102°).

Anal. Calcd. for $C_{22}H_{18}O_4$: C, 76.28; H, 5.24. Found: C, 76.34; H, 5.52.

Summary

A novel oxidative rearrangement of isophorone (IV) to 3,4,5-trimethylphenol (II) and of dihydroisophorone (I) to II and 2,3,5-trimethylphenol (III) by treatment with sulfur trioxide–sulfuric acid plausibly involves sulfonic acid intermediates, of which isophorone-4-sulfonic acid (V) and isophorone-7-sulfonic acid (VI) have been prepared and rearranged under related conditions. The structure of VI has been proved by the synthesis of its hydrogenation product. A mechanism for the rearrangement and aromatization of the sulfonic acids involving a new method of forming carbonium ions is proposed. 4,5-Dimethylresorcinol (XVIII) has been prepared from dimethyldihydroresorcinol by rearrangement of the intermediate 5,5-dimethyldihydroresorcinol-2-sulfonic acid (XVII).

(38) Beilstein, "Handbuch der organische Chemie," Julius Springer, Berlin, 1920, Hauptwerke, 4th ed., Vol. II, p. 684.

(39) Perkin, *J. Chem. Soc.*, **69**, 1457 (1896).

(40) Backer and Strating, *Rec. trav. chim.*, **62**, 66 (1943); Karrer and Schick, *Helv. Chim. Acta*, **26**, 800 (1943).

(41) Simon, *Ann.*, **329**, 306 (1903).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, HARVARD UNIVERSITY]

"α"-Spinasterol

BY LOUIS F. FIESER, MARY FIESER AND RAM NARAYAN CHAKRAVARTI

"α"-Spinasterol[1] is a doubly unsaturated sterol found by Larsen and Heyl[2] to yield a hydrogenation-resistant dihydride that could be isomerized with acid to a Δ^{14}-stenol capable of being hydrogenated to stigmastanol. Fernholz and Ruigh[3] established that the more readily hydrogenable double bond is at the 22,23-position in the side chain, and by hydrogenation of 7-dehydrostigmasterol (I) with palladium catalyst they prepared the $\Delta^{8(14)}$-stenol III and found it identical with the hydrogenation-resistant dihydride from "α"-spinasterol. Fernholz and Ruigh reasoned that the nuclear double bond of "α"-spinasterol is also at the 8,14-position on the basis of their observation that no bond migration occurred when a solution of "α"-spinasterol was shaken with platinum catalyst in the absence of hydrogen (which would attack the side chain). Stavely and Bollenback,[4] however, showed that this evidence is not valid because the characteristic migrations of double bonds from C_7-C_8 or C_8-C_9 to C_8-C_{14} occur only if the catalyst is saturated with hydrogen, an observation confirmed by Barton and Cox.[5] Stavely and Bollenback found that "α"-spinasterol is converted by chromic acid oxidation of the acetate into products analogous to those derived from "α"-dihydroergosterol, and since the latter compound was at the time thought to contain an 8,9-double bond they concluded that "α"-spinasterol is similarly constituted. At about the same time, however, Wieland and

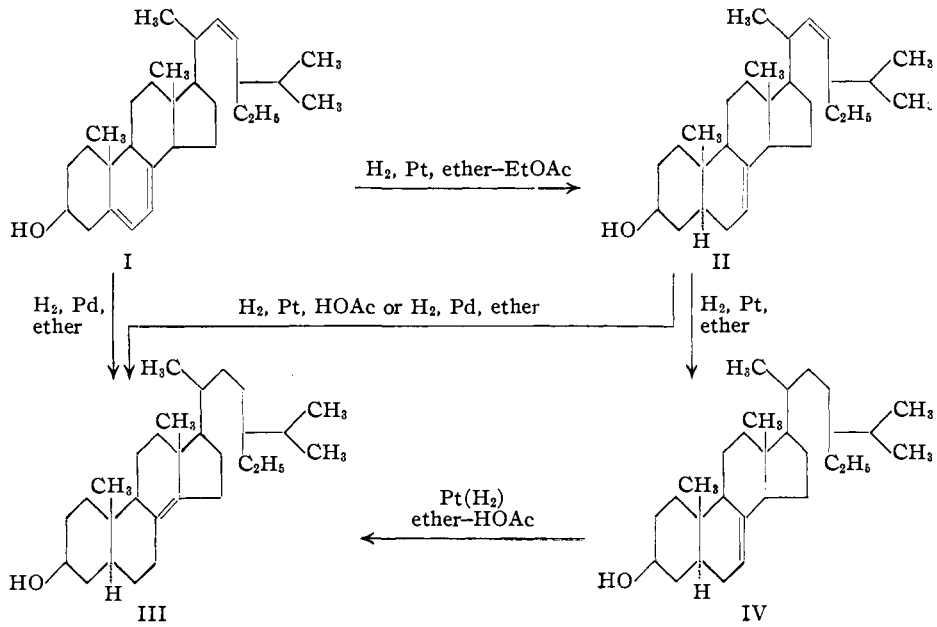
(1) Hart and Heyl, *J. Biol. Chem.*, **95**, 311 (1932); Simpson, *J. Chem. Soc.*, 730 (1937); Dam and co-workers, *Helv. Chim. Acta*, **22**, 313 (1939); Fernholz and M. L. Moore, THIS JOURNAL, **61**, 2467 (1939).

(2) Larsen and Heyl, *ibid.*, **56**, 2663 (1934).

(3) Fernholz and Ruigh, *ibid.*, **67**, 2341 (1945).

(4) Stavely and Bollenback, *ibid.*, **65**, 1600 (1943).

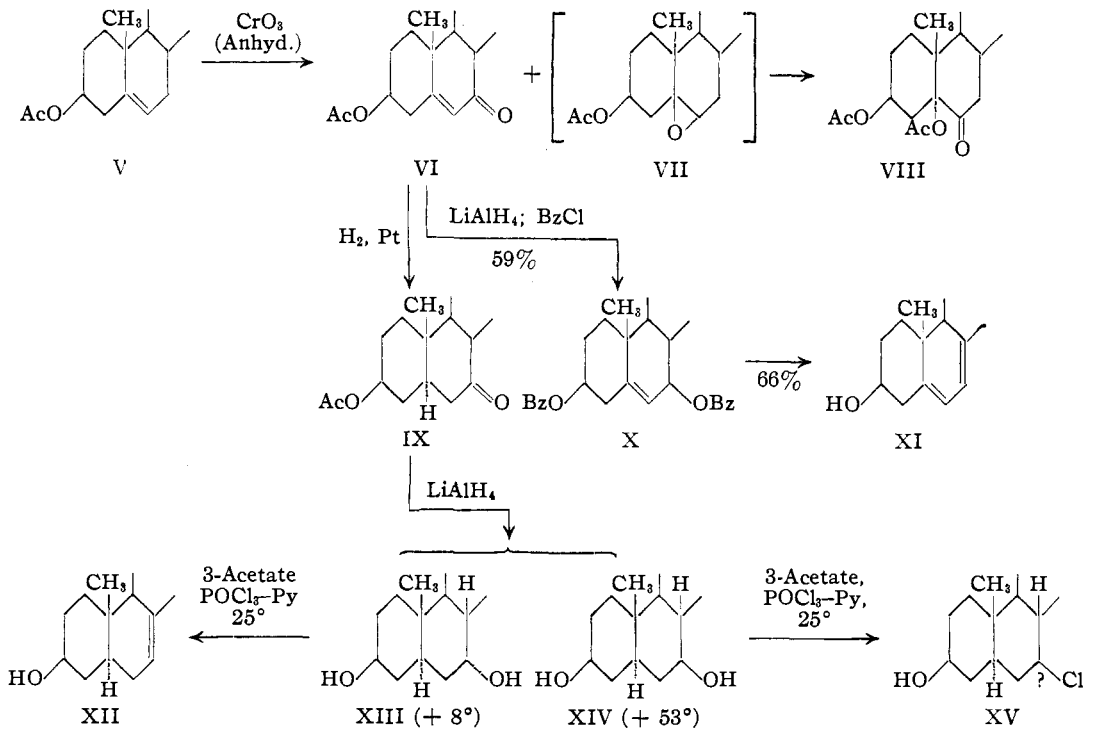
(5) Barton and Cox, *J. Chem. Soc.*, 1354 (1948); we are greatly indebted to Dr. D. H. R. Barton for kindly sending us a copy of the manuscript.



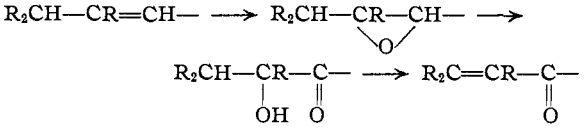
Benend[6] adduced new evidence showing that the nuclear double bond of the comparison compound is actually at the 7,8-position, and Barton and Cox[6] have confirmed their conclusion that the substance is 5-dihydroergosterol. The comparable behavior on oxidation thus suggests the $\Delta^{7,22}$-structure II for "α"-spinasterol. In a brilliant analysis of the optical properties of the various stenols by the method of molecular rotation differences, Barton[7] noted that the optical rotation properties of "α"-spinasterol are indicative of the Δ^{7}-structure II, and more recently Barton and Cox[5] have adduced chemical evidence in support of this structure. Wieland and Benend[6] established that migration of a double bond from the 7,8- or 8,9- to the 8,14-position under the influence of a hydrogen-saturated catalyst occurs in the presence of palladium in neutral or acid medium or with platinum in acetic acid but not with platinum in a neutral medium. Barton and Cox showed that under non-isomerizing conditions (Pt–ether) "α"-spinasterol (II) can be hydrogenated to Δ^{7}-stigmastenol IV, and that this is isomerized to the hydrogenation-resistant $\Delta^{8(14)}$-stenol III under conditions of active catalysis comparable to those employed by Larsen and Heyl (Pt–acid) and by Fernholz and Ruigh (Pd–neutral) for the hydrogenation of "α"-spinasterol. In a parallel investigation completed before we had learned of the work of Barton and Cox, we effected the selective hydrogenation of 7-dehydrostigmasterol (I) under non-isomerizing conditions and found the product II to be identical with "α"-spinasterol. This partial synthesis of the sterol confirms the evidence of Barton and Cox.

7-Dehydrostigmasterol was prepared by an improved procedure worked out in more detail for the preparation of 7-dehydrocholesterol starting with the oxidation of cholesteryl acetate (V) to the 7-ketone (VI).[8] By the usual procedure of oxidation with chromic acid in approximately 90% acetic acid, Windaus obtained the ketone VI in 28% yield, and Buser[9] reports a yield of 26%. By oxidation with chromic anhydride in anhydrous acetic acid[10] and simplification of the procedure, we obtained VI in regularly reproducible yield of 33%. 7-Ketocholesteryl acetate is known to be accompanied by a keto acid resulting from opening of ring B and by cholestane-3β,5α-diol-6-one 3,5-diacetate (VIII).[11] An analogous 5-acetoxy-6-ketone has been isolated from oxidation of the bile acid analog of V,[12] but the side reaction has not heretofore been explained. We suggest that VIII arises through formation of the β-oxide VII and subsequent acetolysis and oxidation. Oxides are known to be formed in the chromic acid oxidation of tetraphenylethylene[13] and 2,4,4-trimethylpentene-1,[14] and of steroids having a double bond between the bridgehead positions C_8-C_9 or C_8-C_{14}.[15] Oxides in which one of the oxido carbon atoms carries a hydrogen atom, as in VII, are very sensitive to chromic acid[16] and are only rarely isolated in oxidations.[17]

(6) Wieland and Benend, *Ann.*, **554**, 1 (1943).
(7) Barton, *J. Chem. Soc.*, 813 (1945).
(8) Windaus, Lettré and Schenck, *Ann.*, **520**, 98 (1935).
(9) Buser, *Helv. Chim. Acta*, **30**, 1385 (1947).
(10) Fieser, THIS JOURNAL, **70**, 3237 (1948).
(11) Schenck, *Z. physiol. Chem.*, **243**, 119 (1936).
(12) Haslewood, *J. Chem. Soc.*, 224 (1938).
(13) Behr, *Ber.*, **5**, 277 (1872).
(14) Byers and Hickinbottom, *Nature*, **160**, 402 (1947); *J. Chem. Soc.*, 1334 (1948).
(15) Petrow, *J. Chem. Soc.*, 998 (1939); Wintersteiner and M. Moore, THIS JOURNAL, **65**, 1513 (1943); Stavely and Bollenback, *ibid.*, **65**, 1285 (1943).
(16) Westphalen, *Ber.*, **48**, 1064 (1915); Ruzicka and Bosshard, *Helv. Chim. Acta*, **20**, 244 (1937).
(17) Petrow and Starling, *J. Chem. Soc.*, 60 (1940).



Such oxides seem to us the likely intermediates in a number of chromic acid oxidations: oxidations like that of "α"-spinasterol acetate[4] in which the double bond changes place and for which we suggest the formulation shown; oxidation of



cholesterol to cholestane-3,6-dione-5α-ol, Δ^4-cholestene-3β-ol-6-one, and Δ^4-cholestene-3,6-dione[18]; oxidation of $\Delta^{3,5}$-cholestadiene to Δ^4-cholestene-3,6-dione.[19,20]

According to the hypothesis presented regarding the oxidation of cholesteryl acetate, the desired allylic oxidation at C_7 competes in part with oxide formation, which probably accounts for the keto acid by-product as well as for VIII, and possibly also with allylic oxidation at C_4, as observed on oxidation with selenium dioxide.[21] Knowledge of the mechanisms of the competing reactions might suggest a means of favoring the one at the expense of the other. Trial oxidations in the presence or absence of oxygen and under illumination or with additives revealed no differential influence.

(18) Mauthner and Suida, *Monatsh.*, **17**, 579 (1896); the first and third substances are indeed known products of the chromic acid oxidation of cholesterol α-oxide (Westphalen[16]).

(19) Windaus, *Ber.*, **40**, 257 (1907).

(20) For formulations, and for references to an alternate hypothesis of initial hydroxylation, see Fieser and Fieser, "Natural Products Related to Phenanthrene," 3rd edition, Reinhold, Publ. Corp., New York, N, Y., 1949.

(21) Rosenheim and Starling, *J. Chem. Soc.*, 377 (1937).

In the original Windaus process for the preparation of 7-dehydrocholesterol the 7-ketone VI was reduced by the Meerwein–Ponndorf method in yield of 30%[8] (Buser[9] reports 20%). We found that reduction with lithium aluminum hydride proceeds more efficiently and more predominately in one steric sense; the chief product was the 7β-hydroxy compound (see below), isolated as the dibenzoate X, and only 5% of the 3β,7α-diol dibenzoate was found present. The 3β,7β-diol dibenzoate X on benzoate cleavage in boiling dimethylaniline solution[12] and hydrolysis afforded 7-dehydrocholesterol in the same yield as reported by Buser.[9]

Wintersteiner and Moore[22] by stepwise hydrogenation of 7-ketocholesteryl acetate and hydrolysis isolated two 7-epimeric cholestane-3,7-diols and assigned to the more abundant and more dextrorotatory epimer the arbitrary designation 7 "α." We isolated the same two substances following reduction of the saturated ketone IX with lithium aluminum hydride. Plattner and Heusser[23] inferred from analogy to 7α- and 7β-hydroxycholanic acids that the more dextrorotatory epimer is actually the 3β,7β-diol XIV. Although we feel that this argument is not valid in the absence of evidence that the difference in the effect of 7α- and 7β-substitution is the same in the cholestane as in the coprostane series, the conclusion of Plattner and Heusser is supported by the following chemical evidence. Wintersteiner and Moore[24] observed that the less dextro-

(22) Wintersteiner and M. Moore, THIS JOURNAL, **65**, 1503 (1943).

(23) Plattner and Heuser, *Helv. Chim. Acta*, **27**, 748 (1944).

(24) Wintersteiner and M. Moore, THIS JOURNAL, **65**, 1507 (1943).

rotatory diol (XIII, as 3-acetate) is more readily dehydrated by *p*-toluenesulfonyl chloride in boiling pyridine than the epimer, and Buser[9] found that the same substance is smoothly dehydrated by phosphorus oxychloride in pyridine at room temperature to Δ^7-cholestenol (XII), an observation that we have confirmed. With a sample of material kindly supplied by Dr. O. Wintersteiner, we investigated the behavior of the more dextrorotatory diol (XIV, as 3-acetate) under the same conditions and found that it is not dehydrated but rather converted into a 7-chloro derivative corresponding to a substance obtained by Wintersteiner and Moore[22] by treatment of XIV-acetate with phosphorus pentachloride; the resistance of the chloro compound to boiling pyridine suggests that it has the 7β-configuration (XV) and is formed without inversion. In view of the known preference for *trans* eliminations, the more easily dehydrated epimer must be the one with the hydroxyl group *trans* to the β-oriented hydrogen atom at C_8 and hence with the 7α-orientation of XIII.

Experimental Part

7-Ketocholesteryl Acetate.[8,9]—Fifteen grams of chromic anhydride was added in small portions during two hours to a vigorously stirred (Hershberg stirrer) solution of 21.4 g. of cholesteryl acetate in 230 cc.[25] of glacial acetic acid with control of the temperature to 53–55°.[26] Stirring was continued for another two hours at the same temperature and then 5 cc. of alcohol was added to destroy the unreacted chromic acid and 150 cc. of the acetic acid was removed by distillation at reduced pressure. The residual solution was diluted with 10 cc.[27] of water and kept overnight for crystallization and the product was then collected, drained thoroughly, washed thrice with cold 80–85% acetic acid (thorough draining) and finally with water. The yield of directly pure 7-ketocholesteryl acetate, m. p. 156–158°, was 6.3 g.

The mother liquor was diluted with water and extracted with ether and the solution washed with ammonia solution and then water and dried and evaporated. Crystallization of the residue from 85% acetic acid gave 1.0 g. more ketone, m. p. 157–158°; total yield 33%.

The yield was exactly the same when the oxidation was conducted at 25–30°, under strong illumination, in an atmosphere of nitrogen, or with addition of dibenzoyl peroxide.

7-Ketostigmasteryl Acetate.[28]—Stigmasteryl acetate (10 g.) in acetic acid (200 cc.) was oxidized by the above procedure except that the reaction mixture was poured into water and the solid product washed and dried in ether. On evaporation of the solution to a small volume and addition of methanol the ketone separated slowly in colorless crystals, m. p. 185°; yield 2.85 g.

7α-[29] and 7β[8,9]-Benzoxycholesteryl Benzoate.—A solution of 8.84 g. (0.02 mole) of 7-ketocholesteryl acetate in 200 cc. of dry ether was added in a thin stream during fifteen to twenty minutes to a stirred ethereal solution of 0.02 mole of lithium aluminum hydride[30] at such a rate as to keep the ether refluxing gently. Stirring was continued for one hour longer and ice-cold dilute sulfuric acid was added very cautiously with stirring to congo red acidity. More ether was added to dissolve the hydroxycholesterol that separated and the solution was dried and evaporated and the residue treated in 35 cc. of pyridine with 18 cc. of benzoyl chloride at 0°. After twenty-four hours the solution was poured onto ice and the viscous oil separated and triturated with methanol, when it solidified. One crystallization from methanol gave 6.3 g. of 7β-benzoxycholesteryl benzoate, m. p. 173–174°.

The methanol mother liquor on evaporation afforded 2 g. of white solid. This was adsorbed on alumina and eluted with petroleum ether–benzene mixtures according to Buser[9] and afforded 1.0 g. of 7β-benzoxycholesteryl benzoate, m. p. 173–174° (total yield, 59%) and 0.6 g. (5%) of 7α-benzoxycholesteryl benzoate, m. p., 158–159°.

7α- and 7β-[28,31] Benzoxystigmasterol Benzoate.—7-Ketostigmasteryl acetate (4.68 g.) was reduced with lithium aluminum hydride and the diol mixture benzoylated by the procedures described immediately above. Two crystallizations of the product from acetone–methanol afforded 3.1 g. of 7β-benzoxystigmasterol benzoate, m. p. 184°, identical with a sample prepared by reduction with aluminum isopropoxide according to Linsert[28] and benzoylation.

The product recovered from the mother liquor was dried thoroughly under suction and chromatographed on alumina with eluent mixtures of petroleum ether (30–60°) and benzene in the ratios 8:1, 4:1, and 1:1. The first fraction afforded a further 0.45 g. of 7β-benzoxystigmasteryl benzoate and the third fraction yielded 0.35 g. of **7α-benzoxystigmasterol benzoate**, which crystallizes from acetone in plates, m. p. 174°.

Anal. Calcd. for $C_{43}H_{56}O_4$ (636.88): C, 81.09; H, 8.88. Found: C, 81.47; H, 9.19.

This dibenzoate is much less soluble in acetone than the epimer, with which it gives a melting point depression. The substance on hydrogenation (Pt) in ether–ethyl acetate solution was found to undergo hydrogenolysis, for the product isolated after acetylation was stigmastanyl acetate.[32]

7α-Hydroxystigmastanyl acetate was prepared by hydrogenation (Pt) of 7-ketostigmasteryl acetate (2.34 g.) in ethyl acetate (30 cc.). The reaction proceeded extremely slowly after absorption of 1.3 moles of hydrogen and so acetic acid (15 cc.) and more catalyst (0.1 g.) were added; the total absorption then reached 3 moles. The product crystallized from methanol containing a little ethyl acetate in shining plates, m. p. 168–170°; yield 1.6 g.

Anal. Calcd. for $C_{31}H_{54}O_3$ (474.74): C, 78.43; H, 11.46. Found: C, 78.55; H, 11.67.

"α"-Spinasterol.—7-Dehydrostigmasteryl benzoate, m. p. 179–180°, was prepared according to Haslewood[31] by refluxing 7β-benzoxystigmasteryl benzoate in dimethylaniline. A suspension of 90 mg. of platinum oxide in 15 cc. of ethyl acetate was reduced completely by shaking with hydrogen, a solution of 610 mg. of 7-dehydrostigmasteryl benzoate in 25 cc. each of absolute ether and ethyl acetate was added, and hydrogenation was continued until the absorption reached 29.7 cc. at 26° (762 mm.) (theory for 1 mole, 29.0 cc.). Two crystallizations of the recovered product from ethyl acetate afforded 300 mg. of

(25) The volume of acetic acid can be reduced to 75 cc., but since the cholesteryl acetate is then not initially all dissolved the reaction period must be extended to eight to ten hours. When this is done distillation of solvent at the end of the reaction is unnecessary and the mixture is diluted directly with 10 cc. of water. When only five hours was allowed for the oxidation (with 75 cc. of solvent) the initial crystallizate (8.6 g., m. p. 138–142°) contained some cholesteryl acetate.

(26) The oxidation is very slow at room temperature and becomes too vigorous above 60°.

(27) The amount of water is critical; if more is used impure material separates but can be purified by crystallization from 85% acetic acid.

(28) Linsert, *Z. physiol. Chem.*, **241**, 125 (1936).

(29) Barr, Heilbron, Parry and Spring, *J. Chem. Soc.*, 1437 (1936) originally designated 7 "β."

(30) About 0.76 g.; the strength of the stock solution was determined by shaking a 1-cc. portion with ether–water and titrating the water layer with standard acid.

(31) Haslewood, *Biochem. J.*, **33**, 454 (1939).

(32) *Cf.* Barr, *et al.*, ref. 29; also Wintersteiner and Ruigh, THIS JOURNAL, **64**, 2453 (1942).

pure "α"-spinasteryl benzoate in large, shining plates, m. p. 200°, $[\alpha]^{25}D$ + 1.8 ± 0.5° (16.8 mg. in 1 cc. chloroform).

Anal. Calcd. for $C_{36}H_{52}O_2$ (516.78): C, 83.66; H, 10.13. Found: C, 84.02; H, 9.94.

A suspension of 100 mg. of the benzoate in 10 cc. of 5% alcoholic sodium hydroxide became clear when refluxed for three to four hours and the filtered solution on cooling deposited 55 mg. of "α"-spinasterol, m. p. 168–169°, $[\alpha]^{25}D$ − 3.6 ± 0.5° (27.9 mg. in 1 cc. chloroform). The substance showed no depression in melting point when mixed with a sample of natural "α"-spinasterol kindly provided by Dr. F. W. Heyl.

"α"-Spinasteryl acetate was prepared by refluxing synthetic "α"-spinasterol (30 mg.) with 0.5 cc. of acetic anhydride for one-half hour. The acetate separated as shining plates on cooling and after recrystallization from acetic acid melted at 186° and gave no depression in melting point with the sample of natural acetate from Dr. Heyl; $[\alpha]^{25}D$ − 4.5 ± 0.5° (19.6 mg. in 1 cc. chloroform).

Anal. Calcd. for $C_{31}H_{50}O_2$ (454.71): C, 81.88; H, 11.06. Found: C, 82.19; H, 10.79.

Reduction of 7-Ketocholestanyl Acetate with Lithium Aluminum Hydride.—The saturated ketone, m. p. 148–149°, was prepared according to Wintersteiner and Moore[22] by partial hydrogenation in ethyl acetate. Reduction of 5.3 g. of material in 75 cc. of ether was conducted as in the previous examples and gave 4.5 g. of product that appeared from the rotation, $[\alpha]D$ + 27°, to be a mixture of about equal parts of the 7-epimers. Separation could not be accomplished by fractional crystallization but was effected by chromatography. Elution of 2 g. of mixture with benzene and then with 4:1 and 2:1 mixtures of benzene–ether gave a gummy first fraction (0.3 g.) followed by a second crystalline fraction (0.7 g., $[\alpha]D$ + 10°) that on one crystallization from methanol gave pure 7α-hydroxycholestanol, m. p. 152°, $[\alpha]^{25}D$ + 8.5° (chloroform). The third fraction gave a crystallizate (0.8 g., $[\alpha]D$ + 46°) that on crystallization from aqueous ethanol afforded 7β-hydroxycholestanol, m. p. 166°, $[\alpha]^{25}D$ + 51°.

Dehydration Experiments with 7-Hydroxycholestanyl Acylates.—In confirmation of the work of Buser,[9] dehydration of 7α-hydroxycholestanyl acetate with phosphorus oxychloride in pyridine was found to give Δ^7-cholestenyl acetate of properties as reported by Buser. When a sample of 200 mg. of 7β-hydroxycholestanyl acetate kindly supplied by Dr. O. Wintersteiner was refluxed for two hours with 4 cc. of dry pyridine and 0.7 cc. of phosphorus oxychloride, the product collected by dilution with ice and water and extraction with ether when crystallized twice from alcohol formed needles, m. p. 118–119° (180 mg.) $[\alpha]^{25}D$ − 23° in chloroform, positive Beilstein test. The substance corresponds in properties to the 7-chlorocholestanyl acetate of Wintersteiner and Moore,[22] m. p. 118–119°, $[\alpha]D$ − 21.7°, obtained with phosphorus pentachloride. The same product was obtained when the reaction mixture was allowed to stand for two days at room temperature.

Plattner and co-workers[33] have described the preparation by pyrolysis of 7α-benzoxycholestanyl acetate of a substance regarded by them as Δ^7-cholestenol, $[\alpha]D$ − 16°, acetate, $[\alpha]D$ − 64°, but differing considerably in optical properties from several substances, including "α"-spinasterol, that we regard as authentic Δ^7-stenols. We converted 7α-hydroxycholestanyl acetate into the 7α-benzoxy derivative (amorphous solid, melts over a range to a clear liquid at 80°) and pyrolyzed this at 8 mm. pressure. The gummy distillate was washed in ether with cold sodium bicarbonate solution and the acid-free residue chromatographed. Elution with 8:1 and 4:1 petroleum ether–benzene mixtures gave in the second fraction a product that formed shining plates from alcohol containing a little acetone (yield about 20%, m. p. 113–114°, $[\alpha]^{25}D$ −31°) (18.3 mg. in 1 cc. chloroform), depression when mixed with Δ^7-cholestenyl acetate (Buser).

Anal. Calcd. for $C_{29}H_{48}O_2$ (428.67): C, 81.25; H, 11.29. Found: C, 81.16; H, 11.26.

The composition is that of a cholestenyl acetate; the substance melts somewhat higher and is distinctly less levorotatory than that reported by Plattner. Further investigation of the substance had to be deferred.

Summary

1. Selective hydrogenation of the 5,6-double bond of 7-dehydrostigmasterol gives a product identical with natural "α"-spinasterol. The synthesis confirms evidence of Barton and Cox that the nuclear double bond is located at C_7-C_8.

2. The Windaus method for the preparation of 7-dehydrocholesterol from cholesteryl acetate has been improved by conducting the oxidation to the 7-ketone under anhydrous conditions and by effecting reduction of the 7-carbonyl group with lithium aluminum hydride.

3. The formation of certain abnormal products in the chromic acid oxidation of unsaturated sterols is attributed to the intermediate formation of oxides.

4. Chemical evidence is presented regarding the configurations of the 7-epimeric hydroxy derivatives of cholesterol and cholestanol.

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(33) Plattner, Heusser, Troxler and Segre, *Helv. Chim. Acta*, **31**, 852 (1948).