with 75 ml. of water and heated to 90°. The solution was chilled and the solid recrystallized from water. The yield of α-chloro-α-*p*-tolylsulfonylacetamide (I) was 1 g. (4.4%), m. p. 162–165°. Repeated recrystallizations from water and alcohol gave α-*p*-tolylsulfonylacetamide.

Reaction of Sodium *n*-Butyl Mercaptide with Dichloroacetamide.—To 10.7 ml. (9 g., 0.10 mole) of *n*-butyl mercaptan was added a sodium ethoxide solution prepared by dissolving 2.3 g. (0.10 gram atom) of sodium in 60 ml. of absolute alcohol. This was added dropwise, at room temperature, to a well stirred solution of 20 g. (0.15 mole) of dichloroacetamide in 150 ml. of absolute alcohol. After the addition the mixture was stirred up for two hours and then allowed to stand for three days. The alcohol was evaporated and the material poured on ice. After several recrystallizations from a mixture of ligroin (b. p. 70–90°) and ether, the product melted at 78–80°. The compound was identified as (bis-*n*-butylthio)-acetamide by oxidation with 15 ml. of 30% hydrogen peroxide in 30 ml. of acetic acid-acetic anhydride mixture (1:1). The oxidation product was shown to be bis-*n*-butylsulfonylacetamide[5] by mixed melting point. The over-all yield was 27% based on the mercaptan.

Reaction of Sodium *p*-Thiocresolate with Dichloroacetamide.—The above experiment was carried out as described for *n*-butylmercaptan using 12.5 g. (0.1 mole) of *p*-thiocresol. The resulting product, m. p. 172–173°, was proved by mixed melting point to be α,α-(bis-*p*-tolylthio)-acetamide.[5] The yield was 88% based on the *p*-thiocresol.

Reaction of α-*p*-Tolylsulfonylacetamide with *t*-Butyl Hypochlorite.—Tertiary butyl hypochlorite was prepared by the method of Taylor, MacMullen and Gammel.[6] To 10.7 g. (0.05 mole) of α-*p*-tolylsulfonylacetamide was added 100 ml. of carbon tetrachloride containing 0.05 mole of *t*-butyl hypochlorite. After heating the mixture for sixty hours on a water-bath 80% of unreacted amide was recovered.

(6) Taylor, MacMullen and Gammel, THIS JOURNAL, **47**, 395 (1925).

Reaction of the Sodium Derivative of α-*p*-Tolylsulfonylacetamide with *p*-Toluenesulfonyl Chloride.—To 2.3 g. (0.1 gram atom) of sodium shot in 225 ml. of benzene was added 7.5 ml. (0.13 mole) of absolute alcohol. The mixture was refluxed until the sodium had dissolved, 21.3 g. (0.1 mole) of α-*p*-tolylsulfonylacetamide added and the mixture refluxed for fifteen minutes. The condenser was set for a downward distillation and 75 ml. of benzene removed. The last portion of the distillate gave a negative test for alcohol with dichromate. To the resulting residue 19.6 g. (0.1 mole) of *p*-toluenesulfonyl chloride in benzene solution was added dropwise with stirring. The material was refluxed for two hours with stirring and was then neutral to moist litmus. The hot solution was filtered and the residue washed with hot benzene. The combined benzene solutions were evaporated to 50 ml., chilled and filtered. The crystals (6 g.) were extracted with hot alcohol and this extract gave after recrystallization 2.5 g. (21% based on the chloride) of a product m. p. 111–112°. This was shown by mixed melting point to be *p*-tolylsulfonyldichloromethane, which is reported[7] to melt at 114°.

The residue from the alcohol extraction was recrystallized from benzene. There was isolated 1 g. (6%) of di-*p*-tolyldisulfone, m. p. 203–205° (dec.). The benzene-insoluble portion of the reaction mixture was crystallized from 5% sodium carbonate solution and gave 11.1 g. (52%) of recovered α-*p*-tolylsulfonylacetamide.

Summary

α-Chloro-α-sulfonylamides have been prepared by the chlorination of α-sulfonylamides in glacial acetic acid. These products contain "positive" chlorine and are considerably more reactive than the α-bromo-α-sulfonylamides previously described.

(7) Otto, *J. prakt. Chem.*, [2] **40**, 526 (1889).

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[CONTRIBUTION FROM THE ANIMAL CHEMISTRY AND NUTRITION SUBSECTION OF IOWA STATE COLLEGE]

The Structure of "7-Dehydrocholestene Isomer"[1]

BY J. C. ECK AND E. W. HOLLINGSWORTH

In a previous paper[2] the crystalline product (m. p. 84–85°, $(\alpha)^{28}D$ + 45.77°), obtained by the action of quinoline on 5,6-dibromocholestane (cholestene dibromide), was considered to be $\Delta^{4,6}$-cholestadiene in a pure condition since the physical properties could not be changed by attempted further purification. However, from more recent research, a considerable accumulation of evidence has been obtained to indicate that no structure other than $\Delta^{4,6}$-cholestadiene could account for the reactions of "7-dehydrocholestene isomer" (m. p. 90–91°, $(\alpha)^{24}D$ + 4.27°). A Wolff–Kishner reduction of the semicarbazone of $\Delta^{4,6}$-cholestadieneone-3, which has been studied by Petrow,[3] yielded a crystalline product (m. p. 82.5–84°, $(\alpha)^{26}D$ − 38.1°) which would also be expected to have the structure of $\Delta^{4,6}$-cholestadiene. As a result of this investigation, it has been found that the 5,6-dibromocholestane-quinoline product is an inseparable

(1) Journal Paper No. J-793 of the Iowa Agricultural Experiment Station, Project No. 506.

(2) Eck, Van Peursem and Hollingsworth, THIS JOURNAL, **61**, 171 (1939).

(3) V. A. Petrow, private communications.

mixture of $\Delta^{4,6}$-cholestadiene and coprostene (pseudo-cholestene), that "7-dehydrocholestene isomer" is $\Delta^{4,6}$-cholestadiene and that the reduction product of $\Delta^{4,6}$-cholestadieneone-3 is an inseparable mixture containing $\Delta^{4,6}$-cholestadiene.

"7-Dehydrocholestene isomer"[1] had originally been found to have a slight positive rotation[4] and from this optical rotation alone it was suggested[5] to be $\Delta^{4,6}$-cholestadiene on the basis that $\Delta^{4,6}$-cholestadiene should also have a positive rotation due to the 4,5-double bond as in coprostene ($(\alpha)_D$ $+64.86°$).[6] At that time $\Delta^{3,5}$-cholestadiene was believed[7] to have a specific rotation of $-63.75°$ which is near the numerical value of the specific rotation of cholestene ($(\alpha)_D$ $-56.29°$)[8]; this would indicate only a slight effect upon optical rotation by the additional double bond in the 3,4-position. However, since the specific rotation of $\Delta^{3,5}$-cholestadiene is now considered[9] to be $-123.23°$ and that of $\Delta^{4,6}$-cholestadiene is $+4.27°$, it is apparent that an additional double bond in either the 3,4- or the 6,7-position effects a considerable increase in levorotation.

"7-Dehydrocholestene isomer" had also been suggested[10] to have a structure in which the double bonds could be located in rings B and C or B and D. However, treatment of "7-dehydrocholestene isomer" or Δ^{5}-cholestenol-7 (7-hydroxycholestene) with dry hydrogen chloride in chloroform was found to yield (practically quantitatively) a hydrocarbon which was shown to be $\Delta^{3,5}$-cholestadiene since it gave no depression in mixed melting point with $\Delta^{3,5}$-cholestadiene, did not yield a maleic anhydride addition product and formed both cholestane and coprostane on catalytic hydrogenation. Such a rearrangement of a conjugated cholestadiene having a double bond in ring C or D should not be expected since the conversion of $\Delta^{5,7}$-cholestadieneol-3 benzoate (7-dehydrocholesterol benzoate) to $\Delta^{7,14}$-cholestadieneol-3 benzoate (dehydrocholesterol B_3 benzoate)[11] by the same reagent involves a rearrangement toward ring D instead of toward ring A. It is interesting in this connection to note that although alcoholic hydrochloric acid[2] converts Δ^{5}-cholestenol-7 to "7-dehydrocholestene isomer" ($\Delta^{4,6}$-cholestadiene), it has now been found that dry hydrogen chloride in chloroform causes a rearrangement of this $\Delta^{4,6}$-cholestadiene to $\Delta^{3,5}$-cholestadiene.

The $\Delta^{4,6}$-cholestadiene structure was indicated for both "7-dehydrocholestene isomer" and the 5,6-dibromocholestane-quinoline product from absorption spectra data and from the catalytic hydrogenation products. The absorption spectra maxima of "7-dehydrocholestene isomer" is located at 238 mμ[4] and that of the 5,6-dibromocholestane-quinoline product is at 247 mμ.[3] These maxima indicated that a conjugated system of double bonds, in which the two double bonds are located in two adjoining rings, is present in both products since no exception has been found to the observation that such structures so far known display maxima around 240 to 250 mμ.[12] Such a structure is supported since a maleic anhydride addition product has not been obtained from either product.[2,4]

Only two ($\Delta^{3,5}$- and $\Delta^{4,6}$-cholestadienes) of the possible conjugated cholestadienes would be expected to yield a mixture of cholestane and coprostane on catalytic hydrogenation and this mixture has been obtained[2] from "7-dehydrocholestene isomer" and from the 5,6-dibromocholestane-quinoline product. The presence of the strongly levorotatory $\Delta^{3,5}$-cholestadiene as a contamination is improbable in either "7-dehydrocholestene isomer" or in the 5,6-dibromocholestane-quinoline product. A conjugated cholestadiene having a double bond in ring C or D should, however, be expected to yield $\Delta^{8,14}$-cholestene on catalytic hydrogenation in analogy with cholesterol[12] and ergosterol[13] derivatives.

Since both "7-dehydrocholestene isomer" and the 5,6-dibromocholestane-quinoline product could not be $\Delta^{4,6}$-cholestadiene although each was indicated to be a pure compound, chemical means were utilized to learn that the 5,6-dibromocholestane-quinoline product is an inseparable mixture. Titration of "7-dehydrocholestene isomer" and of the 5,6-dibromocholestane-quinoline product with perbenzoic acid indicated[2] the presence of two double bonds in each although the lower value observed for the 5,6-dibromocholestane-quinoline product could possibly indicate contamination with a cholestene. This possibility was confirmed by the isolation of coprostene as its

(4) Dimroth and Trautmann, *Ber.*, **69B**, 669 (1936).
(5) Stavely and Bergmann, *J. Org. Chem.*, **1**, 575 (1937).
(6) Mauthner and Suida, *Monatsh.*, **28**, 113 (1907).
(7) Stavely and Bergmann, *J. Org. Chem.*, **1**, 567 (1937).
(8) Mauthner and Suida, *Monatsh.*, **15**, 85 (1894).
(9) Eck and Hollingsworth, *Iowa State College J. Sci.*, **13**, 329 (1939).
(10) Heilbron, Shaw and Spring, *Rec. trav. chim.*, **57**, 529 (1938).
(11) Schenck, Buchholz and Weise, *Ber.*, **69B**, 2696 (1936).
(12) Windaus, Linsert and Eckhardt, *Ann.*, **534**, 22 (1938).
(13) Dithmar and Achtermann, *Z. physiol. Chem.*, **205**, 55 (1932).

dibromide from the 5,6-dibromocholestane-quinoline product. Furthermore, the optical rotation of the 5,6-dibromocholestane-quinoline product ($(\alpha)^{28}D$ +45.77°)[2] is intermediate between that of "7-dehydrocholestene isomer" ($(\alpha)^{24}D$ +4.27°)[2] and of coprostene ($(\alpha)D$ +64.86°)[6] and the specific rotation of the needles obtained by repeated recrystallization of a mixture of these two compounds was found to be +41.7°.

In attempts to prepare $\Delta^{4,6}$-cholestadiene in addition to the previously used[2] method of dehalogenating 5,6-dibromocholestane with quinoline, three other methods were applied which involved the dehydration of Δ^4-cholestenol-7 (pseudo-cholesterol), the ketone reduction of $\Delta^{4,6}$-cholestadieneone-3 and the dehalogenation of 5,6-dibromocholestane with silver nitrate–pyridine. Dehydration of Δ^4-cholesten-7-ol by heat treatment with activated alumina yielded a slightly dextrorotatory hydrocarbon which gave no depression in mixed melting point with "7-dehydrocholestene isomer." However, dehydration at higher temperatures yielded products which had lower melting points and greater levorotation and whose constants could not be appreciably changed by attempted purification (similar observations in purification have been found in the case of cholesterilene.[9,14]

In a manner similar to the reduction of $\Delta^{3,5}$-cholestadieneone-7 (oxycholesterilene) to a product ($(\alpha)D$ −63.75°) referred to as $\Delta^{3,5}$-cholestadiene,[7] a Wolff–Kishner reduction of the semicarbazone of $\Delta^{4,6}$-cholestadieneone-3 yielded a crystalline product which was not found possible to purify. The reduction product was, however, indicated to contain "7-dehydrocholestene isomer" since the same cholestenedione was isolated from chromic acid oxidation product. This reduction product was found to be similar to a product which was obtained by the action of silver nitrate–pyridine on α-5,6-dibromocholestane (α-cholestene dibromide) in a manner similar to the conversion of 4,5-dibromocoprostane (pseudocholestene dibromide) to a product ($(\alpha)D$ −68.7°) referred to as $\Delta^{3,5}$-cholestadiene.[15]

Additional support for the location of the double bonds of "7-dehydrocholestene isomer" in rings A and B was indicated from the formation of coprostene by the ketone reduction of the oxidation product of "7-dehydrocholestene isomer." Chromic acid oxidation of "7-dehydrocholestene isomer" yielded a cholestenedione of an unknown structure which may be Δ^5-cholestenedione-4,7 in analogy with the similar oxidation of cholesterilene ($\Delta^{3,5}$-cholestadiene) to Δ^4-cholestenedione-3,6 (oxycholestenone).[16] The disemicarbazone of this cholestenedione on Wolff–Kishner reduction in the presence of a small amount of hydrazine hydrate[17] yielded a crystalline product from which coprostene was isolated. The formation of coprostene is not irreconcilable with the suggested structure of the cholestenedione since the Wolff–Kishner reductions of both $\Delta^{4,6}$-cholestadieneone-3 and $\Delta^{3,5}$-cholestadieneone-7 do not yield pure products.

Experimental

Treatment of "7-Dehydrocholestene Isomer" with Hydrogen Chloride.—Dry hydrogen chloride gas was passed into a solution of 200 mg. of "7-dehydrocholestene isomer" dissolved in 15 cc. of chloroform at 0° for three hours. The solvent was removed *in vacuo* (distillation under the reduced pressure of a water pump) and the residue was crystallized from acetone–methanol to yield 160 mg. of a product in the form of needles, m. p. 77–79°, $(\alpha)^{22}D$ −99.8° (c = 2.11 in CCl_4), which was shown to be $\Delta^{3,5}$-cholestadiene since it gave no depression in mixed melting point with $\Delta^{3,5}$-cholestadiene,[2] did not yield a maleic anhydride addition product and formed both cholestane and coprostane on catalytic hydrogenation.

Treatment of Δ^5-Cholestenol-7 with Hydrogen Chloride.—Dry hydrogen chloride gas was passed into a solution of 300 mg. of Δ^5-cholestenol-7 dissolved in 15 cc. of chloroform at room temperature for four hours. The solvent was removed *in vacuo* and the residue dissolved in 25 cc. of petroleum ether (Skelly B) was passed through an 18 × 40 mm. column of activated alumina (freshly heated 50 to 200 mesh Alorco). The column was washed with 50 cc. of petroleum ether and the combined filtrates were concentrated *in vacuo*. The residue was crystallized from acetone–methanol to yield 170 mg. of a product in the form of large needles, m. p. 77.5–79°, $(\alpha)^{20}D$ −101.1° (c = 1.87 in CCl_4), which was shown to be $\Delta^{3,5}$-cholestadiene since it gave no depression in mixed melting point with $\Delta^{3,5}$-cholestadiene,[2] did not yield a maleic anhydride addition product and formed both cholestane and coprostane on catalytic hydrogenation.

Bromination of the 5,6-Dibromocholestane-quinoline Product.—A slight excess of bromine in glacial acetic acid was added to a solution of 25 mg. of the 5,6-dibromocholestane-quinoline product dissolved in ether. After standing for two minutes, 4 drops of acetone was added and the solution was allowed to stand in the refrigerator for several days until crystals formed which melted at 114–116° and gave a mixed melting point of 114–116° with an authentic sample of 4,5-dibromocoprostane (coprostene dibromide), m. p. 115–116°.

(14) Eck and Van Peursem, *Iowa State College J. Sci.*, **13**, 115 (1939).

(15) Hattori, THIS JOURNAL, **60**, 3082 (1938).

(16) Fantl and Kabos, *Monatsh.*, **47**, 251 (1926).

(17) Dutcher and Wintersteiner, THIS JOURNAL, **61**, 1992 (1939).

Dehydration of Δ^4-Cholestenol-7.—An intimate mixture of 0.5 g. of Δ^4-cholestenol-7 and 0.5 g. of activated alumina (200 mesh) was heated at 250–255° for two hours. The resulting mixture was extracted with 25 cc. of petroleum ether and passed through an 18 × 40 mm. column of activated alumina (50 to 200 mesh). The column was washed with 50 cc. of petroleum ether and the combined filtrates were concentrated *in vacuo*. The residue was crystallized from alcohol to yield 95 mg. of a product in large needles, m. p. 84–87°, $(\alpha)_D$ 0°, which after four recrystallizations from alcohol melted at 88–89° and $(\alpha)^{24}_D$ was +1.05 (c = 2.77 in CCl_4). The product gave no depression in mixed melting point with a sample of "7-dehydrocholestene isomer."

An intimate mixture of 0.3 g. of Δ^4-cholestenol-7 and 0.5 g. of activated alumina (200 mesh) was heated at 295–305° for one hour and 0.1 g. of a product was obtained in a manner similar to that described above. After repeated recrystallization the needles melted at 74–76° and $(\alpha)^{24}_D$ was −38.0°. A solution of 50 mg. of this product dissolved in 15 cc. of alcohol containing 4 drops of concentrated hydrochloric acid was refluxed for two hours and the product recovered in needles melted at 75–77° and $(\alpha)^{23}_D$ was −40.5°.

A mixture of 0.2 g. of Δ^4-cholestenol-7, 0.3 g. of anhydrous copper sulfate and 6 cc. of xylene was refluxed for eight hours. To the reaction mixture was added 20 cc. of petroleum ether and this was then decanted through a 18 × 28 mm. column of activated alumina (50 to 200 mesh). The column was washed with 30 cc. of petroleum ether and the combined filtrates were concentrated *in vacuo*. The residue was recrystallized from alcohol to yield 0.13 g. of a product in the form of needles which melted at 80–82° and $(\alpha)^{25}_D$ was −9.8° (c = 2.00 in CCl_4).

Reduction of $\Delta^{4,6}$-Cholestadieneone-3.—A mixture of 2.8 g. of the semicarbazone of $\Delta^{4,6}$-cholestadieneone-3 and 2.8 g. of sodium in 28 cc. absolute alcohol was heated in a sealed tube at 200° for eight hours. The reaction product was dissolved in ether and the ether solution was washed with water, dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was dissolved in 30 cc. of petroleum ether and passed through a 18 × 105 mm. column of petroleum ether, the combined filtrates were concentrated *in vacuo* and the residue was crystallized from acetone–methanol to yield 1.1 g. of well formed needles, m. p. 77–79°, $(\alpha)^{24}_D$ −47.0° (c = 3.00 in CCl_4). The melting point and optical rotation gradually changed during the course of twenty-three recrystallizations from acetone–methanol to yield a product which melted at 82.5–84° and $(\alpha)^{26}_D$ was −38.1° (c = 2.15 in CCl_4).

Oxidation of the Hydrocarbon from $\Delta^{4,6}$-Cholestadieneone-3.—The above reduction product from $\Delta^{4,6}$-cholestadieneone-3 (0.6 g.) was oxidized with chromic acid according to the method of Fantl and Kabos[16] and 15 mg. of a product was obtained, by crystallization from ether–methanol, in the form of plates, m. p. 157–158°, which gave no depression in mixed melting point with a sample of the cholestenedione obtained by the chromic acid oxidation of "7-dehydrocholestene isomer."

Treatment of α-5,6-Dibromocholestane with Silver Nitrate–Pyridine.—A mixture of 2 g. of α-5,6-dibromocholestane, 50 cc. of pyridine and 7.5 g. of silver nitrate was allowed to stand at room temperature in the dark for one month. Most of the pyridine was removed *in vacuo* and the residue was dissolved in ether. The ether solution was filtered to remove the silver bromide and washed with dilute hydrochloric acid and with water. The ether solution was then dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was dissolved in 50 cc. of petroleum ether and the solution was passed through a 18 × 65 mm. column of activated alumina. The column was washed with 150 cc. of petroleum ether and the combined filtrates were concentrated *in vacuo*. The residue was repeatedly recrystallized from acetone–methanol to yield 1.1 g. of large halogen-free needles, m. p. 81–83°, $(\alpha)^{22}_D$ −58.1° (c = 1.72 in CCl_4). This product possessed properties similar to the product obtained by the Wolff–Kishner reduction of $\Delta^{4,6}$-cholestadieneone-3.

Oxidation of "7-Dehydrocholestene Isomer."—"7-Dehydrocholestene isomer" (3.5 g.) was oxidized with chromic acid according to the method of Fantl and Kabos[16] to yield 0.75 g. of a cholestenedione in pale yellow plates, m. p. 150–153°, which after several recrystallizations from alcohol melted at 160–161° and $(\alpha)^{21}_D$ was −51.7° (c = 1.02 in CCl_4) (disemicarbazone, m. p. 322° with decomposition).

Anal. Calcd. for $C_{27}H_{42}O_2$: C, 81.34; H, 10.63. Found: C, 81.22, 81.16; H, 10.83, 10.76. Calcd. for $C_{29}H_{48}O_2N_6$: N, 16.39. Found: N, 16.63.

Reduction of the Cholestenedione from "7-Dehydrocholestene Isomer."—The disemicarbazone of the cholestenedione obtained by the chromic acid oxidation of "7-dehydrocholestene isomer" (0.45 g.) was heated with a solution of 0.50 g. of sodium in 9 cc. of absolute alcohol and 0.3 cc. of 40% hydrazine hydrate in a sealed tube at 200° for eight hours. The reaction mixture was dissolved in ether and the ether solution was washed with water, dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was dissolved in 20 cc. of petroleum ether and passed through a 9 × 35 mm. column of activated alumina. The column was washed with 20 cc. of petroleum ether and the combined filtrates were concentrated *in vacuo*. The residue was recrystallized from alcohol to yield 80 mg. of short needles, m. p. 70–71°, which after seven recrystallizations from alcohol melted at 75–76°. The mixed melting point with an authentic sample of coprostene (m. p. 77–78°) was 76–78°, indicating the identity of the two samples. The identity was further verified by brominating the hydrocarbon to yield plates, m. p. 114–115°, which melted at 114.5–116° when mixed with an authentic sample of coprostene dibromide, m. p. 115–116°.

Summary

The product obtained by the action of quinoline on 5,6-dibromocholestane is indicated to be an inseparable mixture of $\Delta^{4,6}$-cholestadiene and coprostene. "7-Dehydrocholestene isomer" is indicated to be $\Delta^{4,6}$-cholestadiene. The Wolff–Kishner reduction product of the semicarbazone of $\Delta^{4,6}$-cholestadieneone-3 is indicated to be an inseparable mixture containing $\Delta^{4,6}$-cholestadiene.

The specific rotation of $\Delta^{4,6}$-cholestadiene is

therefore +4.27°. An additional double bond in the 3,4-position in cholestene or in the 6,7-position in coprostene effects a considerable increase in levorotation.

$\Delta^{4,6}$-Cholestadiene was found to be rearranged to $\Delta^{3,5}$-cholestadiene by treatment with dry hydrogen chloride in chloroform.

AMES, IOWA RECEIVED SEPTEMBER 11, 1940

[CONTRIBUTION FROM THE G & A LABORATORIES, INC.]

On the Dehydration of 22-Dihydrostigmasterol and Cholesterol with Iodine

BY TORSTEN HASSELSTROM AND BURT L. HAMPTON

The catalytic dehydration with iodine of secondary alcohols yields in most cases unsaturated hydrocarbons. Hibbert,[1] suggests that the action of iodine on alcohols proceeds with the formation of alkyl iodide and hypoiodite, which may react together to cause the formation of an ether and free iodine. While such a reaction apparently does not occur with ordinary monobasic secondary alcohols as a normal course of reaction, we have observed that such an ether formation takes place in the sterol series, without apparent formation of the expected unsaturated hydrocarbons.

Cholesterol and 22-dihydrostigmasterol were heated at an elevated temperature with about 5% of iodine, yielding di-cholesterol ether and di-22-dihydrostigmasterol ether, respectively, together with iodides of apparently the same type as Montignie[2] obtained on treating cholesterol at 100° with about 20% of iodine in benzene solution. The 22-dihydrostigmasterol used in this work was prepared from sulfate pulp tallol; the di-22-dihydrostigmasterol ether and dicholesterol ether obtained were identified, respectively, by their tetrabromides.

Acknowledgment.—Thanks are due to Professor Marston T. Bogert of Columbia University, New York City, for permitting us to study his notes on the catalytic action of iodine on organic compounds.

Experimental

Dicholesterol Ether.—The cholesterol used was obtained by the hydrolysis with alcoholic potassium hydroxide of cholesteryl acetate with subsequent recrystallization; m. p. 150–151° (cor.); $(\alpha)_D$ −38.8° (in chloroform).

Ten grams of cholesterol was heated for two hours at 170–180° with 5% of iodine, the iodine being added slowly during the first ten minutes of heating. After three extractions of the reaction mass with boiling ethanol, from which 2.3 g. of cholesterol was recovered, the residue was dissolved in hot ethyl acetate and the solution allowed to stand overnight whereupon a white crystalline material separated out. After four recrystallizations from ethyl acetate, the material melted constantly at 198–199° (cor.); $(\alpha)_D$ −52° (in chloroform); yield 0.8 g. or 8.5%.

Anal. Calcd. for $C_{54}H_{90}O$: C, 85.93; H, 12.02. Found: C, 85.65; H, 12.07.[3]

The mother liquor from the first ethyl acetate crystallization was evaporated to dryness leaving six grams of a red oil which would not crystallize. This oil contained iodine as shown by a sodium fusion, and apparently was identical with the oil obtained by Montignie[2] by the action of iodine on cholesterol in benzene solution.

Tetrabromide of Dicholesterol Ether.—0.20 gram of dicholesterol ether was dissolved in 15 ml. of chloroform and 0.5 g. of bromine dissolved in 10 ml. of chloroform added. The solution was allowed to stand for thirty minutes, the chloroform and excess bromine removed *in vacuo*, and the resulting solid recrystallized from ethyl acetate containing a little benzene, m. p. 178–179° (cor.).

Anal. Calcd. for $C_{54}H_{90}Br_4O$: C, 60.36; H, 8.44. Found: C, 60.60; H, 8.56.

22-Dihydrostigmasterol.—The procedure followed is an improvement of the method described by Hasselstrom[4] for the separation of fatty and resin acids of tallol.

1000 grams of crude sulfate pulp tallol, 1000 cc. of methanol and 100 cc. of concentrated sulfuric acid (sp. gr. 1.84), were refluxed for one hour, then cooled and shaken with two liters of 10% salt solution and 2000 cc. of benzene. The benzene layer was separated and shaken with an excess of 1% sodium hydroxide solution until the resin acids were removed. The benzene solution was washed with water, the benzene removed by distillation at ordinary temperature and the residue fractionated in vacuum; yield 438 g. of methyl ester of fatty acids of tallol, b. p. 192–210° at 6 mm. pressure, and 290 g. of residue.

256 grams of the above residue was saponified for one and one-half hours with 1300 cc. of a 10% potassium hydroxide solution. The alkaline solution was extracted three times with ether, the ether solution was washed with water and finally dried over anhydrous sodium sulfate. After evaporation of the ether, there was obtained a semi-solid residue which after two recrystallizations from ethanol melted at 123–128° (uncor.), yield 14.5 g. After several crystallizations from ethanol, the melting point of the 22-

(1) Hibbert, THIS JOURNAL, **37**, 1748 (1915).

(2) Montignie, *Bull. soc. chim.*, **53**, 1412 (1933).

(3) All analyses by Mr. S. Gottlieb, Columbia University, New York City.

(4) Hasselstrom, *Paper Trade J.*, **83** [2], 60 (1926).