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73. Saburo Akagi: Bromo Derivatives of Cholestenone. (2).[1]

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In the preceding paper, it was shown that oxidation of cholesta-3,5-dien-7-one (Ⅶ) with perphthalic acid gave the 3α,4α-epoxide (I). On treatment with hydrogen bromide in acetic acid, (I) was converted to 4-bromocholesta-3,5-dien-7-one (Ⅷ). On the other hand, (I) was converted to bromohydrin (Ⅱ) on treatment with hydrobromic acid in acetone solution. It was difficult to purify the bromohydrin (Ⅱ) and was directly submitted to acetylation or benzoylation. The acetate (Ⅲa) of (Ⅱ) was obtained as easily purified product of m.p. 107°, with an absorption maximum at 245 mμ, and the benzoate (Ⅲb) of (Ⅱ) was obtained as a product of m.p. 133°, with an absorption maximum at 230 mμ and an inflexion at 240 mμ. When (Ⅲa) was treated with zinc dust in boiling ethanol, it was converted to cholesta-3,5-dien-7-one, which was also obtained by its reduction with Raney nickel W-2 in dioxane, since 3α-acetoxyl group was eliminated easily.[2] When (Ⅲa) was shaken with Raney nickel in acetic acid without hydrogen stream at room temperature, cholest-5-en-7-one (Ⅳ) was obtained and attempts to obtain 3α-hydroxycholest-5-en-7-one acetate were without success. It is known that oxidation of cholest-2-ene[3] with perbenzoic acid gives an α-epoxide, whose catalytic hydrogenation gives cholestan-3α-ol. However, 3α,4α-epoxycholest-5-en-7-one (I) was converted to cholestan-7-one (V) by hydrogenation of the epoxide with Raney nickel W-4 and (I) was also reduced by lithium aluminum hydride, a small amount of cholesta-2,4,6-triene being obtained.

Treatment of 3α-hydroxy-4β-bromocholest-5-en-7-one benzoate (Ⅲb) or acetate (Ⅲa) with hydrochloric acid in ethanol eliminated the benzoyloxyl or acetoxyl group readily, and gave 4-bromocholesta-3,5-dien-7-one (Ⅷ). On boiling with pyridine or collidine for a few hours, (Ⅲb) was converted to 6-bromocholesta-3,5-dien-7-one (Ⅵ) in a good yield. It is noteworthy that bromine migrates from C-4 to C-6 by treatment with a base such as pyridine or collidine. In the preceding paper,[1] it was reported that treatment of 4-bromo-7-oxocholesteryl benzoate with pyridine resulted in migration of bromine from C-4 to C-6 and the attempt was made to confirm this fact by further experiment.

When cholesta-3,5-dien-7-one (Ⅶ) was treated with one mole of bromine at room temperature, it was converted to 3,4-dibromocholest-5-en-7-one (Ⅺ), m.p. 125° (decomp.), with an absorption maximum at 245 mμ (ε 11,100). The constants given in Tables I and Ⅱ for this dibromo-ketone showed that it is an α,β-unsaturated ketone, and addition of bromine occurred in the first step to the double bond at 3—4, since addition of bromine to 7-oxocholesteryl acetate at 5—6 did not proceed at room temperature, and on heating at 50°, it was converted to a dibromo compound in a poor yield. The dibromo-ketone (Ⅺ) is, therefore, assumed to be 3α,4β-dibromocholest-5-en-7-one. When (Ⅺ) was treated by refluxing in pyridine, 6-bromocholesta-3,5-dien-7-one (Ⅵ) was obtained in a good yield. In this case also, bromine at C-4 migrated to C-6. The bromine migration like this was also observed on preparing 4,6-dibromocholesta-3,5-dien-7-one (ⅩⅥ) obtained by Jackson and Jones.[4] Addition of one mole of bromine to the olefinic bond of 4-bromocholesta-3,5-dien-7-one (Ⅷ) gave a tribromide, m.p. 147° (decomp.), with absorption maxima at

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2) A. Windaws, J. Naggatz: Ann., **542**, 204 (1939).
3) A. Fürst, Pl. A. Plattner: Helv. Chim. Acta, **32**, 275 (1949).
4) H. Jackson, E.R.H. Jones: J. Chem. Soc., **1940**, 659.

263 mμ (ε 10,720) and at 1718 (-CO) and 1595 (C=C) cm^{-1}, indicative of the presence of $\Delta^{5,7}$-one system without a substituent in C-6. Thus, the tribromide would be 3,4,4-tribromocholest-5-en-7-one (XII) and not 3,4,6-tribromocholest-5-en-7-one assigned by Jackson and Jones.[4] When 6-bromocholesta-3,5-dien-7-one (VI) was treated with one mole of bromine, it was converted to a different tribromide, 3,4,6-tribromocholest-5-en-7-one (XIV), m.p. 124°, with absorption maximum at 273 mμ (ε 7,040). Treatment of 3,4,6-tribromocholest-5-en-7-one (XIV) with pyridine gave the debrominated product, 6-bromocholesta-3,5-dien-7-one (VI) in a quantitative yield, but treatment of 3,4,4-tribromocholest-5-en-7-one (XII) with pyridine gave a dibromo-dienone in a good yield, with absorption maximum at 305 mμ, indicating a bathochromic shift of about 27 mμ from that of cholesta-3,5-dien-7-one. Its infrared absorptions at 1610 and 1563 cm^{-1} due to C=C bond showed a great decrease in frequency by 21 and 38 cm^{-1}, respectively, from that of cholesta-3,5-dien-7-one, and it is similar to the case of 6-bromocholesta-3,5-dien-7-one. From these observation, the dibromo-dienone is assumed to be 4,6-dibromocholesta-3,5-dien-7-one (XVI) as assigned by Jackson and Jones, and the migration of bromine from C-4 to C-6 was also observed.

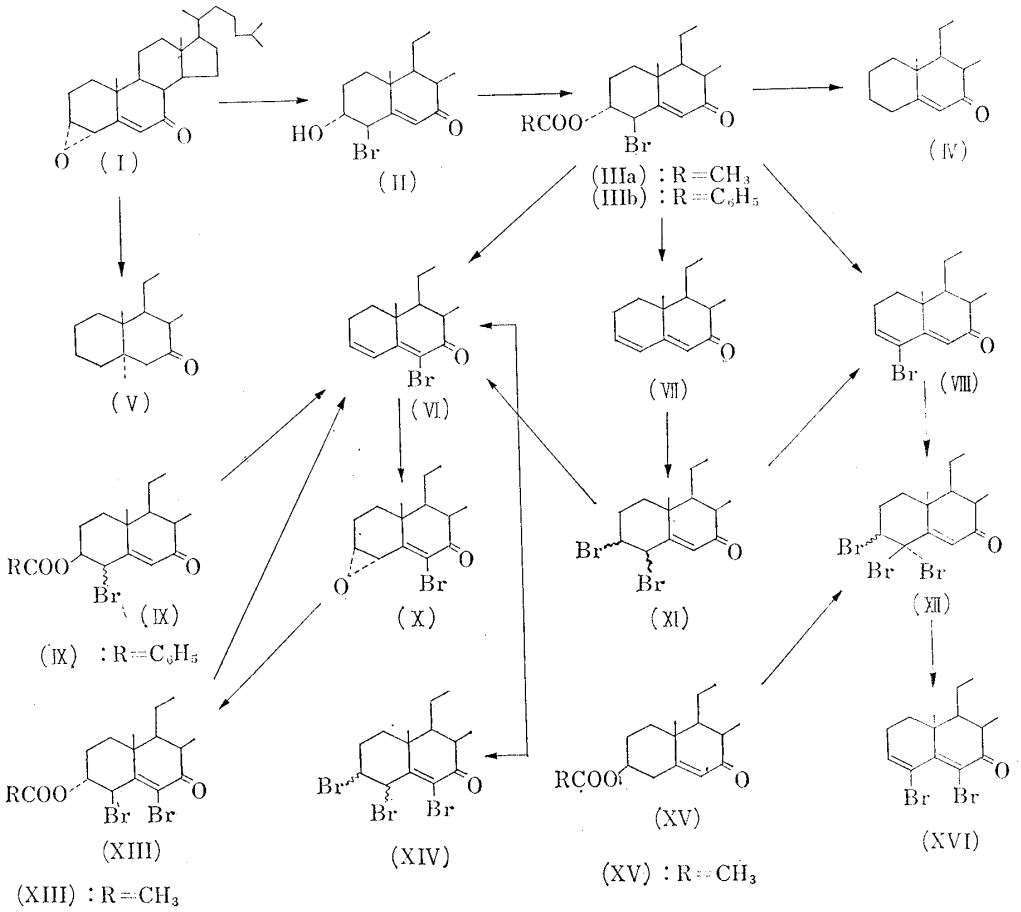

Chart 1.

From the results of above four experiments (III→VI, IX→VI, XI→VI, and XII→XVI) it is noted that treatment of cholest-5-en-7-one without substituent at C-6, but substituted at C-4 with bromine and at C-3 with bromine or acyloxyl group, with a base such as pyridine or collidine gave 6-bromocholesta-3,5-dien-7-one accompanied by bromine migration from C-4 to C-6. If the reaction proceeded further, it would be expected to form a pyridinium bromide at first, then degradation of pyridinium salt and elimination of

acyloxyl group would occur at the same time accompanied by migration of bromine, since 3-acyloxy-6-bromocholest-5-en-7-one, which is the supposed reaction intermediate, is not obtained. Ultraviolet absorption of above bromo-ketones is shown in Table I in comparison with that of the parent ketone. The data cited in Table I show that in bromo-substituted cholest-5-en-7-ones bathochromic shift of about 7 mμ is observed due to bromine substituted at C-4 and about 15 mμ due to bromines disubstituted at the same position. It is assumed that such a bathochromic shift is effected by the orientation of substituted bromine at C-4, because bromine at C-4 in (Ⅲ) and (XI) is probably β-oriented and in cholest-4-en-3-one an axial 6β-bromo substituent has some bathochromic effect of about 5 mμ,[5] not apparent in chloro compound.[6]

Similarly, in 6-bromocholest-5-en-7-one derivatives, substitution of bromine at C-5 effects a bathochromic shift of about 18~23 mμ and substitution of bromine at C-4 in 6-brominated monoënone effect a more bathochromic shift of about 15 mμ. In the case of cholesta-3,5-dien-7-one derivatives, substitution of bromine at C-6 effects a bathochromic shift of about 17 mμ, substitution at C-4, about 5 mμ, and disubstitution at C-4 and C-6, about 27 mμ. Values of molecular extinction coefficient decrease in parallel with the number of bromines substituted.

Infrared absorptions of above bromo-ketone are shown in Table Ⅱ. As was reported in the preceding paper, bromine substitution at C-4, as in (Ⅲ) and (XI), decreases the intensity of C=C stretching band, bromine at C-6, as in (Ⅵ), (X), (XIV), (XV), and (XIII), produces a characteristic shift of C=C and C=O stretching band, and a strong shift of C=O stretching band was observed in (XII).

Treatment of 6-bromocholesta-3,5-dien-7-one (Ⅵ) with perphthalic acid gave a 3,4-epoxide, which is converted to a bromohydrin with hydrogen bromide in acetic acid. The reaction product was acetylated in the usual way with acetic anhydride and pyridine. Resulting acetyl derivative of bromohydrin is asssigned the structure of 3α-acetoxy-4β,6-dibromocholest-5-en-7-one (XII), since its acetoxyl group is eliminated very readily as was the case in 3α-acetoxy-4β-bromocholest-5-en-7-one, and its ultraviolet absorption (Table I) shows the above-mentioned bathochromic shift of about 15 mμ, which is assumed to be characteristic of 4β-bromo substituents.

Table I. Ultraviolet Absorptions of Bromo Derivatives of Cholesten-7-one

Compound	λ_{max}^{EtOH} mμ	Δ mμ	ε	Δε
Cholest-5-en-7-one	238		13,950	
4-Bromocholest-5-en-7-one	245	+ 7	12,100	−1,850
3α-Hydroxy-4β-bromocholest-5-en-7-one acetate	245	+ 7	11,880	−2,070
3,4-Dibromocholest-5-en-7-one	245	+ 7	11,100	−2,850
3,4,4-Tribromocholest-5-en-7-one	263	+15	10,720	−3,230
4-Anilinocholest-5-en-7-one	245, 286	+ 7	21,090, 4,605	
3α,4α-Epoxycholest-5-en-7-one	239	+ 1	11,680	
3β-Hydroxy-6-bromocholest-5-en-7-one acetate[a]	256		10,500	
3α,4α-Epoxy-6-bromocholest-5-en-7-one	262	+ 6	9,660	− 840
3,4,6-Tribromocholest-5-en-7-one	273	+17	7,040	−3,460
3α-Hydroxy-4,6-dibromocholest-5-en-7-one acetate	271	+15	9,870	− 630
Cholesta-3,5-dien-7-one	278		24,250	
6-Bromocholesta-3,5-dien-7-one	295	+17	17,790	−6,460
4-Bromocholesta-3,5-dien-7-one	283	+ 5	17,900	−6,350
4-Anilinocholesta-3,5-dien-7-one	251, 281	+ 3	17,850, 19,110	
4,6-Dibromocholesta-3,5-dien-7-one	305	+27	12,300	−11,950

a) K. Takeda, T. Komeno : This Bulletin, **4**, 432 (1956).

5) L. Ruzicka, W. Bosshard, W.H. Fischer : Helv. Chim. Acta, **19**, 1147 (1936).
6) D.H.R. Barton, E. Miller : J. Am. Chem. Soc., **72**, 1066 (1950).

Table II. Infrared Absorptions of Bromo Derivatives of Cholesten-7-one

Compound	C=O Stretching vibrations (cm^{-1})			C=C Stretching vibrations (cm^{-1})	
	ester	-CO-	Δ(C=O)	-C=C	Δ(C=C)
3β-Hydroxycholest-5-en-7-one acetate	1733	1675		1634	
3α-Hydroxy-4β-bromocholest-5-en-7-one acetate	1748	1681	+ 6	1626 w	− 8
3β-Hydroxycholest-5-en-7-one benzoate*	1712	1668		1634	
3α-Hydroxycholest-5-en-7-one benzoate	1724	1678	+10	1621 w	−13
3,4-Dibromocholest-5-en-7-one		1675		1623 w	−11
3,4,4-Tribromocholest-5-en-7-one		1718		1595	
Cholesta-3,5-dien-7-one		1661		1631	
				1601	
6-Bromocholesta-3,5-dien-7-one		1684	+23	1623	− 8
				1558	−43
4-Bromocholesta-3,5-dien-7-one		1675	+14	1614	−17
				1592	− 9
4,6-Dibromocholesta-3,5-dien-7-one*		1689	+28	1610	−21
				1563	−38
3β-Hydroxy-6-bromocholest-5-en-7-one acetate*	1730	1685		1595	
3α-Hydroxy-4,6-dibromocholest-5-en-7-one acetate	1742	1698	+13	1572	−23
3,4,6-Tribromocholest-5-en-7-one		1692	+ 7	1575	−20
3α,4α-Epoxy-6-bromocholest-5-en-7-one		1690		1605	

* Values in $CHCl_3$, others in Nujol.

Experimental*2

3α-Hydroxy-4β-bromocholest-5-en-7-one Benzoate (IIIb) and Acetate (IVa)——To a suspension of 10 g. of 3α,4α-epoxycholest-5-en-7-one in 120 cc. of Me_2CO, 14 cc. of HBr (sp. gr. 1.48) was added. The resulting yellow solution was allowed to stand for 1.5 hr., H_2O was added, and the separated precipitate was collected by filtration. The product weighed 11 g., which was benzoylated or acetylated directly. A solution of 1 g. of the product in 3 cc. of pyridine was treated with 1 cc. of BzCl, allowed to stand for 3 hr. at room temperature, MeOH was added, and allowed to stand overnight with cooling. The separated crystalline product was collected by filtration and recrystallized from Me_2CO to 0.7 g. of prisms, m.p. 133~133.5°. $[\alpha]_D^{25}$ −136° (c=1.0, $CHCl_3$). UV : λ_{max}^{EtOH} 230 mμ (ε 28,400), inflexion at 240 mμ. *Anal.* Calcd. for $C_{34}H_{47}O_3Br$: C, 69.99; H, 8.06; Br, 13.71. Found : C, 69.77; H, 7.77; Br, 13.64.

A mixture of 1 g. of the bromohydrin, 2 cc. of pyridine, and 1 cc. of Ac_2O was allowed to stand for 2 hr. at room temperature. The reaction mixture was added with MeOH and a small amount of H_2O, and allowed to stand with cooling. The separated product was collected by filtration, boiled with Me_2CO, filtered while hot, and the filtrate was added with MeOH. The separated product was collected by filtration and crystallized from Et_2O-MeOH to 0.4 g. of needles, m.p. 107~108°. $[\alpha]_D^{25}$ −102° (c=1.0, $CHCl_3$). *Anal.* Calcd. for $C_{29}H_{45}O_3Br$: C, 66.90; H, 8.64; Br, 15.35. Found : C, 66.88; H, 8.84; Br, 15.43.

Reduction of 3α-Hydroxy-4β-bromocholest-5-en-7-one Acetate (IIIa) and Benzoate (IIIb)——a) A mixture of 0.25 g. of 4β-bromocholest-5-en-7-one benzoate and 2 g. of Zn dust in 10 cc. of EtOH was refluxed for 2 hr. The hot solution was filtered, Zn dust was washed with benzene, and the combined solution was evaporated *in vacuo* to almost dryness. The solid residue was heated with MeOH, filtered while hot, concentrated to a small volume, and cooled. The crystalline substance was collected by filtration, and recrystallized from EtOH to 0.15 g. of leaflets, m.p. 111~112°. It was identified with cholesta-3,5-dien-7-one by mixed melting point and the infrared spectrum.

b) Hydrogenation of 0.5 g. of 3α-hydroxy-4β-bromocholest-5-en-7-one acetate in 30 cc. of dioxane with 1 g. of Raney Ni W-2 in atmospheric pressure at room temperature gave 0.2 g. of cholesta-3,5-dien-7-one.

c) A solution of 0.5 g. of 3α-hydroxy-4β-bromocholest-5-en-7-one acetate in 20 cc. of AcOH was shaken with 1 g. of Raney Ni W-2 without H_2 stream. The reaction proceeded with a little foaming. After 40 min., the reaction mixture was filtered to remove the catalyst, H_2O was added, and the product was collected by filtration, which was recrystallized twice from EtOH to leaflets, m.p. 125~126°. The product did not depress the melting point of cholest-5-en-7-one and showed identical

*2 All melting points are not corrected.

infrared spectrum as that of cholest-5-en-7-one. *Anal.* Calcd. for $C_{27}H_{44}O$: C, 84.36; H, 11.45. Found : C, 83.86; H, 11.02. UV : λ_{max}^{EtOH} 238 mμ (ε 12,500).

Hydrogenation of 3α,4α-Epoxycholest-5-en-7-one (I)——A solution of 1 g. of (I) dissolved in 40 cc. of dioxane, with Raney Ni W-4 as the catalyst, was hydrogenated until about 2 moles of H_2 had been absorbed. After removal of the catalyst, the filtrate was evaporated in a reduced pressure and the solid residue crystallized from EtOH to 0.6 g. of leaflets, m.p. 110~113°. Further purification from EtOH-MeOH gave a product of m.p. 114~115°. This was identified with cholestan-7-one by mixed melting point and the infrared spectrum.

3ξ,4ξ-Dibromocholest-5-en-7-one (XI)——To a suspension of 2 g. of cholesta-3,5-dien-7-one in 10 cc. of AcOH, 5 cc. of Br_2 solution (solution of 4 cc. of Br_2 in 60 cc. of AcOH) was added at room temperature. The red color disappeared at once. To the reaction mixture, 40 cc. of MeOH was added and the separated oily substance solidified gradually on standing in the refrigerator. After cool, the solid was collected by filtration and recrystallized twice from Et_2O-MeOH to 1 g. of needles, m.p. 120~123°(decomp.). $[\alpha]_D^{25}$ −119°(c=1.01, $CHCl_3$). *Anal.* Calcd. for $C_{27}H_{41}OBr_2$: C, 59.77; H, 7.74; Br, 29.52. Found : C, 59.36; H, 7.73; Br, 29.52.

6-Bromocholesta-3,5-dien-7-one (VI)——a) A solution of 15 g. of 3,4-dibromocholest-5-en-7-one (XI) in 100 cc. of pyridine was refluxed for 3.5 hr. The brown reaction mixture was evaporated *in vacuo*, MeOH was added, the separated crystalline substance was collected by filtration after cool, and recrystallized from EtOH-benzene to 10 g. of yellow leaflets, m.p. 147~149°. On further recrystallization from EtOH, discolored with activated carbon, the product formed white leaflets, m.p. 148~150°. $[\alpha]_D^{25}$ −306°(c=1.01, $CHCl_3$). *Anal.* Calcd. for $C_{27}H_{41}OBr$: C, 70.28; H, 8.89; Br, 17.35. Found: C, 70.28; H, 9.00; Br, 17.13. UV : λ_{max}^{EtOH} 295 mμ (ε 19,880). The infrared spectrum of the product was identical with that of 6-bromocholesta-3,5-dien-7-one.

b) A solution of 1 g. of 3α-hydroxy-4β-bromocholest-5-en-7-one benzoate (IIIb) in 6 cc. of pyridine was refluxed for 6 hr. The reaction mixture was evaporated *in vacuo*, MeOH was added, and the separated crystalline product was collected by filtration after standing overnight with cooling. Deep yellow substance (0.8 g.) was obtained, which showed ultraviolet absorption maximum at 295 mμ. The product was dissolved in benzene, discolored over a small amount of alumina, the effluent was evaporated, and the solid residue was recrystallized twice from EtOH-benzene to leaflets, m.p. 148~149°. This was identified with the above-mentioned 6-bromocholesta-3,5-dien-7-one. Heating of (IIIb) with methyl-ethyl-pyridine for 1 hr. at 120° gave the same product, 6-bromocholesta-3,5-dien-7-one, in a good yield.

c) A solution of 0.5 g. of 3,4,6-tribromocholest-5-en-7-one (XIV) in 15 cc. of pyridine was refluxed for 2 hr. The reaction mixture was treated in the same manner as for (a). The product (0.3 g.), identified with 6-bromocholesta-3,5-dien-7-one, was obtained.

4-Bromocholesta-3,5-dien-7-one (VIII)——a) A mixture of 0.5 g. of 3α-hydroxy-4β-bromocholest-5-en-7-one benzoate (IIIb), 0.5 cc. of conc. HCl, and 2 cc. of dioxane in 10 cc. of EtOH was refluxed for 1.5 hr. The resulting yellow solution was evaporated *in vacuo* to separate an oily substance, which was cooled to deposit a crystalline product. The product isolated by filtration was recrystallized from EtOH to 0.2 g. of needles, m.p. 118~120°. UV : λ_{max}^{EtOH} 283 mμ (ε 17,800). This was identified with 4-bromocholesta-3,5-dien-7-one by mixed melting point and the infrared spectrum.

b) To a solution of 0.5 g. of 3,4-dibromocholest-5-en-7-one (XI) in 20 cc. of AcOH, 0.5 cc. of a solution of HBr in AcOH (10%) was added. After standing for 2 days at room temperature, the brown reaction mixture was diluted with H_2O and the precipitated oily product showed an ultraviolet absorption maximum at 283 mμ. The oily product was dissolved in petr. ether-benzene (1:1) and chromatographed over alumina. The first fraction (100 cc.) gave 0.15 g. of a crystalline product which was chromatographed again over alumina. After two recrystallizations from MeOH, 30 mg. of a product was obtained (m.p. 118~120°) which did not depress the melting point of 4-bromocholesta-3,5-dien-7-one obtained as in procedure (a).

3,4,4-Tribromocholest-5-en-7-one (XII)——To a solution of 0.5 g. of 4-bromocholesta-3,5-dien-7-one in 2 cc. of $CHCl_3$, 1.3 cc. of Br_2 solution (1 cc. of Br_2 was dissolved in 30 cc. of $CHCl_3$) was added. The reaction mixture was added with MeOH under ice-cooling and the separated precipitate solidified at once. The product was collected by filtration and recrystallized twice from $CHCl_3$-AcOH to 0.3 g. of needles, m.p. 147°(decomp.). UV : λ_{max}^{EtOH} 263 mμ (ε 10,720). $[\alpha]_D^{26}$ −126°(c=1.02, $CHCl_3$). This was identified by mixed melting point and the infrared spectrum with the compound obtained by Jackson and Jones.[4]

4,6-Dibromocholesta-3,5-dien-7-one (XVI)——A solution of 1.2 g. of 3,4,4-tribromocholest-5-en-7-one in 5 cc. of pyridine was refluxed for 1 hr. Resulting black solution was evaporated *in vacuo* to dryness which was triturated with MeOH. The crystalline product isolated by filtration was recrystallized from EtOH to 0.1 g. of needles, m.p. 186~187°, which showed an ultraviolet absorption maximum at 305 mμ. The product was identified by mixed melting point and the infrared spectrum with the compound obtained by Jackson and Jones.[4]

3α,4α-Epoxy-6-bromocholest-5-en-7-one (X)——To a solution of 3 g. of 6-bromocholesta-3,5-dien-7-one in 10 cc. of $CHCl_3$, 77 cc. of Et_2O solution of perphthalic acid (containing 4.7 g. of perphthalic acid) was added and the mixture was allowed to stand at room temperature for 48 hr. Et_2O solution was decanted from precipitated perphthalic acid, combined with Et_2O washings, washed with $NaHCO_3$ solution and H_2O, dried, and evaporated to dryness. The resulting oily residue was added with 30 cc. of MeOH-EtOH mixture and allowed to stand overnight in a refrigerator. The crystalline product isolated by filtration was recrystallized from Et_2O-EtOH to 1.5 g. of plates, m.p. 125~131°. Further purification from Et_2O-EtOH gave white plates, m.p. 133°. $[\alpha]_D^{25}$ −150°(c=1.00, $CHCl_3$). *Anal.* Calcd. for $C_{27}H_{41}O_2Br$: C, 67.92; H, 8.59; Br, 16.77. Found : C, 67.94; H, 8.45; Br, 16.65. UV : λ_{max}^{EtOH} 262 mμ (ε 9,660).

3α-Hydroxy-4β,6-Dibromocholest-5-en-7-one Acetate (XIII)——To a suspension of 3.6 g. of 3α,4α-epoxy-6-bromocholest-5-en-7-one (X) in 36 cc. of AcOH, 10 cc. of AcOH solution of HBr (28%) was added and the mixture was allowed to stand for 35 min. at room temperature. Resulting dark yellow solution was diluted with H_2O and the separated crystalline product was collected by filtration. Crude bromohydrin (3.4 g.) was obtained. A solution of 1 g. of this product in 4 cc. of pyridine was acetylated with 4 cc. of Ac_2O. After standing overnight, the reaction mixture was placed in ice-water and the product isolated by filtration was recrystallized from EtOH-benzene to 0.6 g. of prisms, m.p. 160~162°(decomp.). Further recrystallization from EtOH-benzene gave colorless prisms, m.p. 161~166°(decomp.). $[\alpha]_D^{25}$ +72°(c=1.0, $CHCl_3$). *Anal.* Calcd. for $C_{29}H_{44}O_3Br_2$: C, 58.01; H, 7.33; Br, 26.17. Found : C, 58.26; H, 7.35; Br, 26.55. UV : λ_{max}^{EtOH} 271 mμ (ε 9,870).

Hydrogenation of 3α-Hydroxy-4β,6-dibromocholest-5-en-7-one Acetate (XIII)——A solution of 0.5 g. of 3α-hydroxy-4β,6-dibromocholest-5-en-7-one acetate (XIII) in 40 cc. of dioxane, with Raney Ni W-2 as a catalyst, was hydrogenated until about 1 mole of H_2 had been absorbed. After removal of the catalyst, the filtrate was evaporated *in vacuo* to almost dryness. The solid residue (0.4 g.) was recrystallized twice from EtOH-benzene to white leaflets, m.p. 148~149°. The product was identified by mixed melting point and the infrared spectrum with 6-bromocholesta-3,5-dien-7-one.

3,4,6-Tribromocholest-5-en-7-one (XIV)——To a suspension of 2 g. of 6-bromocholesta-3,5-dien-7-one in 6 cc. of AcOH and 6 cc. of CCl_4, 4 cc. of AcOH solution of Br_2 (4 cc. of Br_2 dissolved in 60 cc. of AcOH) was added, MeOH was added to the resulting clear solution until turbid, and the separated oily substance solidified gradually on cooling. After standing for 24 hr., the crystalline product isolated by filtration was recrystallized twice from Et_2O-MeOH to 1.5 g. of leaflets, m.p. 122~124°. $[\alpha]_D^{25}$ +40°(c=1.00, $CHCl_3$). *Anal.* Calcd. for $C_{27}H_{41}OBr_3$: C, 52.27; H, 6.61; Br, 38.70. Found : C, 52.04; H, 6.57; Br, 38.70. UV : λ_{max}^{EtOH} 273 mμ (ε 7,040).

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Summary

Fission of 3α,4α-epoxycholest-5-en-7-one with hydrobromic acid gave a bromohyrin, whose acyloxyl derivatives were converted to 4-bromocholesta-3,5-dien-7-one, particularly to 6-bromocholesta-3,5-dien-7-one accompanied with bromine migration. Also, 3,4-dibromocholest-5-en-7-one was converted to 6-bromocholesta-3,5-dienone. The ultraviolet and infrared absorption spectra of these bromo derivatives were summarized.

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