
VIII] Reaction of Neutral or Alkaline Reagent on α-Camphene—The following mixtures (1) to (5) were maintained each at 130° for 5 hrs. in sealed tubes. No effect, however, was found, only unreacted raw material being recovered.

1) A mixture of 1 g. of α-camphene, 0.5 g. of KBr, and 3 cc. of abs. EtOH.
2) A mixture of 1 g. of α-camphene, 0.2 g. of CaCl₂, and 5 cc. of abs. EtOH.
3) A mixture of 1 g. of α-camphene, 0.5 g. of AcOK, and 5 cc. of abs. EtOH.
4) A mixture of 1 g. of α-camphene, 1 g. of KOH, and 5 cc. of abs. EtOH.
5) A mixture of 1 g. of α-camphene enolated in hexane by the addition of Na line and warming, and 10 cc. of abs. EtOH.

Summary

The positions of the double bonds in α-campholic acid-I and -II were determined by investigating their respective oxidation products, confirming thereby the results obtained by the spectrum method. An attempt was also made to clarify the process of conversion from 10-bromocamphor into α-campholic acid, proving it to be a straight reaction without passing through any intermediates such as α-camphene.

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In 1938, Barr and Heilbron obtained a dibromide, m.p. 177°, by dibromination of 7-oxocholestanyl acetate (Ia), which was presumed to be 6,6-dibromo compound by comparison of the bromination velocity of each epimer of 6-monobromides. In 1954, Cookson discussed the ultraviolet absorptions of α-substituted bromo-oxosteroids and deduced that the above dibromide would be 6α,8β-dibromide from the fact that the contribution of axial bromine is considerably higher than that of the gem-dibromide. We re-examined Heilbron’s experiments and obtained a dibromide (IIa), m.p. 183–185°(decomp.), which agrees nearly well with the Heilbron’s dibromide in respect to the melting point, crystal form, and ultraviolet spectrum, but differs a little in optical rotation (see Table I). It seems that from the optical data, the Heilbron’s dibromide was contaminated with 6β-monobromide, and these dibromides are assumed to be identical. Dibromination of 7-oxocholestanyl benzoate (Ib) also gave a dibromide (IIb), m.p. 163–165°.

The dibromination reactions proceed very easily in the 7-oxocholestane series, but it is somewhat difficult in the 7-oxocholanic acid series and the reactions tend to stop at a monobromide. Further bromination of methyl 3α,12α-diacetoxy-6α-bromo-7-

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oxocholane in chloroform gave no dibromide, but direct bromination of methyl 3α,
12α-diacetoxy-7-oxocholane (VII) with excess bromine in glacial acetic acid gave a
substance (VIII), m.p. 149~151° (decomp.), in a poor yield. This substance is assumed
to be a molar mixture (or molecular compound) of monobromide and dibromide from
the results of the elemental analysis. The ultraviolet and infrared absorption data of
these brominated compounds together with those of the parent ketones are summarized
in Table II.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{max}^{\text{UV}}$</th>
<th>$\log{\varepsilon}$</th>
<th>$\Delta m$</th>
<th>$\nu_{\text{max}}^{\text{Nujol}}$ (cm$^{-1}$)</th>
<th>$\Delta$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7-Oxocholesteryl acetate (Ia)</td>
<td>287</td>
<td>1.60</td>
<td></td>
<td>1730, 1709</td>
<td></td>
</tr>
<tr>
<td>6,6-Dibromo-7-oxocholesteryl acetate (IIa)</td>
<td>302</td>
<td>2.08</td>
<td>+15</td>
<td>1730, 1724</td>
<td>+15</td>
</tr>
<tr>
<td>7-Oxocholesteryl benzoate (Ib)</td>
<td></td>
<td></td>
<td></td>
<td>1708</td>
<td></td>
</tr>
<tr>
<td>6,6-Dibromo-7-oxocholesteryl benzoate (IIb)</td>
<td></td>
<td></td>
<td></td>
<td>1717</td>
<td>+19</td>
</tr>
</tbody>
</table>

It is generally known that one of the bromine atoms is eliminated very easily in
the case of the 2,2-dibromo-3-oxosteroids.$^3$ The dehydrobromination reaction of (IIa)
or (IIb) also occurred very readily. Though (IIa) was not affected by sodium iodide
in acetone, refluxing of (IIa) with silver acetate in glacial acetic acid gave a bromine-

3) A. L. Wilds, C. Djerassi: J. Am. Chem. Soc., 68, 2125(1946); C. Djerassi, C. R. Scholy: ibid.,
69, 2404(1947); J. Org. Chem., 13, 697(1948); J. J. Beereboom, C. Djerassi: J. Org. Chem., 19,
1196(1954).
containing product (IVa), m.p. 171~173°. A bromine-containing product (IVb), m.p. 213~215°, was also obtained from (IIb) by boiling in pyridine for 10 minutes. Similarly, refluxing of (VII) in pyridine for 10 minutes gave a product (IX), m.p. 230~232° (decomp.), which also contains one bromine atom. Another unsaturated bromo compound (V), m.p. 153~155°, was isolated by a long treatment of (IIa) with several dehydrogenation reagents, such as boiling collidine, silver acetate-glacial acetic acid, silver nitrate-pyridine or potassium hydroxide-methanol. This compound was also obtained by refluxing of (IIb) in pyridine for a long time. Table III summarizes the ultraviolet data of these bromides with each parent unsaturated ketone. Djerassi reported that α-bromine substitution of α,β-unsaturated ketones resulted in a bathochromic shift of approximately 23 mμ in the ultraviolet absorption and it is assumed from the data cited in Table III that (IVa), (IVb), and (IX) possess a partial structure of 6-bromo-Δ₈-en-7-one.

Table III. Ultraviolet Absorptions of α-Bromo-Substituted α,β-Unsaturated Ketones (in EtOH)

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ_{max}^{EtOH}</th>
<th>ε</th>
<th>Δλ</th>
<th>Δ log ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>7-Oxocolesterol acetate</td>
<td>235°</td>
<td>4.08</td>
<td>+21</td>
<td>-0.06</td>
</tr>
<tr>
<td>6-Bromo-7-oxocolesterol acetate (IVa)</td>
<td>256</td>
<td>4.02</td>
<td>260</td>
<td>4.12</td>
</tr>
<tr>
<td>7-Oxocolesterol benzoate (VI)</td>
<td>230</td>
<td>4.22</td>
<td>+30</td>
<td>-0.01</td>
</tr>
<tr>
<td>6-Bromo-7-oxocolesterol benzoate (IVb)</td>
<td>260</td>
<td>4.11</td>
<td>277°</td>
<td>4.39</td>
</tr>
<tr>
<td>7-Oxo-Δ₈-h-cholestadiene (III)</td>
<td>295°</td>
<td>4.25</td>
<td>+19</td>
<td>-0.14</td>
</tr>
<tr>
<td>6-Bromo-7-oxo-Δ₈-cholestanol (V)</td>
<td>259</td>
<td>3.96</td>
<td>+23</td>
<td>-0.18</td>
</tr>
<tr>
<td>Et 3α,12α-Diacetoxy-7-oxo-Δ₈-cholestanate</td>
<td>236</td>
<td>4.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Me 3α,12α-Diacetoxy-6-bromo-7-oxo-Δ₈-cholestanate (IX)</td>
<td>259</td>
<td>3.96</td>
<td>+23</td>
<td>-0.10</td>
</tr>
</tbody>
</table>


As mentioned above, (V) was obtained from either (IIa) or (IIb). From this fact, together with its analytical values and ultraviolet absorption data, the structure of (V) must be represented as 6-bromo-Δ₈-h-cholestadien-7-one, caused by the elimination of acyloxy group at C₃. Acetoxy group at C₃ appears to be eliminated more easily than benzoxyloxy group in the same position under the above-mentioned conditions.

A compound having the same structure was isolated by Jackson and Jones from the tribromide of 7-oxocolesterol acetate by the action of sodium iodide in acetone, but the physical properties of this compound and of the present compound are quite different with respects to the melting point (the former, m.p. 117°; the latter, m.p. 155°) and the ultraviolet absorption (λ_{max}^{EtOH} the former, 288 mμ, (log ε 4.25); 344 mμ (log ε 2.2); the latter, 295 mμ (log ε 4.25)). As Dorfman pointed out, Jackson's compound is not likely to have this structure from the results of the ultraviolet absorptions. Refluxing of (IVb) with zinc dust in alcohol gave the known 7-oxocolesterol benzoate (VI). The attempt to effect rearrangement of (V) with warm hydrogen bromide-acetic acid was unsuccessful, and only gave the known 7-oxo-Δ₈-h-cholestadiene (III). These results also give further support to each structure in the chart.

Table IV summarizes the infrared absorptions of these bromo-enones with each parent unsaturated ketone. In this case, α-bromine substitution also causes a shift.

### Table IV. Infrared Absorptions of α-Bromo-substituted α,β-Unsaturated Ketones (in CHCl₃)

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν\textsubscript{max} (acet. or ester) (7-ketone) (cm⁻¹)</th>
<th>ν\textsubscript{max} (C=O) (cm⁻¹)</th>
<th>Δν\textsubscript{C=O} (cm⁻¹)</th>
<th>ν\textsubscript{max} (C=\textsubscript{α}-C\textsubscript{β}) (cm⁻¹)</th>
<th>Δν\textsubscript{C=\textsubscript{α}-C\textsubscript{β}} (cm⁻¹)</th>
<th>Δν\textsubscript{C=\textsubscript{β}-C\textsubscript{γ}} (cm⁻¹)</th>
<th>Δν\textsubscript{C=\textsubscript{γ}-C\textsubscript{δ}} (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7-Oxocholesteryl acetate</td>
<td>1730</td>
<td>1667</td>
<td>+18</td>
<td>1595</td>
<td>-42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-Bromo-7-oxocholesteryl acetate (IVa)</td>
<td>1712</td>
<td>1668</td>
<td></td>
<td>1634</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7-Oxocholesteryl benzoate (VI)</td>
<td>1712</td>
<td>1668</td>
<td></td>
<td>1595</td>
<td>39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7-Ox-\textsuperscript{α},\textsuperscript{β}-cholastadiene (III)</td>
<td>1633</td>
<td>+18</td>
<td>1596</td>
<td>1626</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-Bromo-7-oxo-\textsuperscript{α},\textsuperscript{β}-cholastadiene (V)</td>
<td>1672</td>
<td>+21</td>
<td>1558</td>
<td>-38</td>
<td>1618</td>
<td>-8</td>
<td></td>
</tr>
<tr>
<td>Et 3\textsuperscript{α},12\textsuperscript{α}-Diacetoxo-7-oxo-\textsuperscript{α},\textsuperscript{β}-cholesterolene (RI)</td>
<td>1730*</td>
<td>1664*</td>
<td></td>
<td>1626*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Et 3\textsuperscript{α},12\textsuperscript{α}-Diacetoxo-6-bromo-7-oxocholesterolene (RI)</td>
<td>1720*</td>
<td>1686*</td>
<td>+22</td>
<td>1590*</td>
<td>-36</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{†} Value in Cs\textsubscript{2}. \textsuperscript{*} Values in Nujol.

Generally in α-substituted bromo-oxosteroids, the ultraviolet absorption band shows a bathochromic shift (ca. 25 mμ) due to the axial bromine substitution, while the infra-red absorption band indicates a hypsochromic shift (ca. 20 cm⁻¹) due to the equatorial bromine substitution.\textsuperscript{8} The data cited in Table II show that the dibromide (IIa or IIb) has an axial and equatorial bromine atoms and will be 6,6-\textit{gem}- or 6α,8β-dibromide. Cookson’s arguments\textsuperscript{3} on Heilbron’s dibromide are based on the amount of contribution of an axial bromine only in the ultraviolet absorptions of α-bromo substituted oxosteroids and he used the point of inflexion as the absorption maximum of 2,2-dibromocholestanone. In this case, it will be necessary to consider not only the contribution of an axial bromine but the contribution of an equatorial one. Consideration of additional contribution of an axial and an equatorial bromine atom indicates that the Δ value (m\textsubscript{α} of bromo-oxosteroid—m\textsubscript{α} of oxosteroid) of (IIa) and (IIa) is +15 mμ, far less than the Δ value (+25 mμ) of 5α,7β-dibromo-6-oxocholestan-2\textsuperscript{α} acetate. Both the Δ value and the above-stated chemical experiments support the structure of 6,6-dibromo-7-oxocholestan-2\textsuperscript{α} acetate for (IIa) rather than 6α,8β-dibromide.\textsuperscript{9}

Heating of (IIa) or (IIb) with collidine in a sealed tube for 8 hours gave a bromine-free yellow compound, m.p. 120\°, in a poor yield, as a by-product of (V). The fact that (V) is not affected under such a drastic dehydrohalogenation reaction gives further support for the vinyl bromide structure of (V). The results of elemental analysis and ultraviolet absorption spectrum (λ\textsubscript{max} 239, 278, 330 mμ) of the yellow compound are in close agreement with those of 4\textsuperscript{α},5\textsuperscript{β},6\textsuperscript{γ},7-oxocholestatristiene, the dehydrohalogenation product obtained by Karrer\textsuperscript{8} and Djerassi\textsuperscript{11} from the bromide of 4\textsuperscript{α},5\textsuperscript{β},6\textsuperscript{γ},7-oxocholestatristiene.

The authors are grateful to Messrs. Ieki and Miyahara, Miss Morita, and Mrs. Koyama for elemental analysis, and to Mr. Matsui for infrared spectral measurements.

8) K. Takeda, K. Igarashi, T. Konomo: This Bulletin, 2, 34(1954), and refs. cited in the report.

\* It is generally known that the infrared spectra of the conjugated diene-type compounds give two absorption bands caused by symmetrical and asymmetrical stretching vibrations. The absorption bands in question may also be referred to these stretching vibrations.
Experimental

7-Oxo-6,6-dibromocholesteryl Acetate (IIa)—To a mixture of 4 g. of 7-oxocholesteryl acetate (Ia) in 40 cc. of CCl₄ containing a few drops of BF₃-etherate, 2.9 g. of Br₂ was added and allowed to stand at room temp. for 3 days. The solution was washed with water, aq. Na₂CO₃ solution, and water, dried over Na₂SO₄, and evaporated to dryness in vacuo. The residue was recrystallized from acetone to give 3.7 g. of leaflets (IIa), m.p. 183~185°C (decomp.); $\lambda_{\text{max}}^{\text{Nujol}}$ 302 mp (log $\varepsilon$ 2.98); $\nu_{\text{max}}^{\text{Nujol}}$ 1730, 1709, 1236 cm⁻¹; $\nu_{\text{max}}^{\text{Nujol}}$ +13.8 ± 2.5°C (c=0.88125, l=1, a=0.122, CHCl₃). Anal. Calcd. for C₃₀H₄₀O₂Br₅: C, 57.81; H, 7.70; Br, 26.53. Found: C, 58.03; H, 7.25; Br, 26.02.

7-Oxo-6,6-dibromocholesteryl Benzoate (IIb)—Similar treatment of 5 g. of 7-oxocholesteryl benzoate (Ib) in 100 cc. of CHCl₃ containing a few drops of BF₃-etherate and 3.2 g. of Br₂ yielded 5 g. of prismatic needles (IIb), m.p. 163~165°C; $\nu_{\text{max}}^{\text{Nujol}}$ 1717, 1269 cm⁻¹. Anal. Calcd. for C₃₀H₄₂O₂Br₅: C, 61.45; H, 7.28; Br, 24.05. Found: C, 61.25; H, 7.24; Br, 24.21.

Impure Methyl 3a,12a-Diacetoxy-6,6-dibromo-7-oxocholanate (VIII)—To a mixture of 2 g. of methyl 3a,12a-diacetoxy-7-oxocholanate (VIII) in 40 cc. of glacial AcOH containing a few drops of BF₃-etherate, 1.4 g. of Br₂ was added and warmed at 50°C on a steam bath for 20 hrs. The solution was not decolorized and poured into water. The precipitate was collected by filtration and dissolved in ether. The ether solution was washed with aq. Na₂CO₃ solution and water, dried over Na₂SO₄, and evaporated to dryness. The residue was crystallized from ether and recrystallized several times from MeOH to give 500 mg. of plates (VIII), m.p. 149~151°C (decomp.). Anal. Calcd. for C₂₉H₂₉O₂Br₂: C, 56.13; H, 6.91; Br, 18.91.  Found: C, 55.76; H, 7.25; Br, 18.86.

To a mixture of 2 g. of methyl 3a,12a-diacetoxy-6,6-dibromo-7-oxocholanate in 20 cc. of CHCl₃ containing a few drops of BF₃-etherate, 0.7 g. of Br₂ was added and allowed to stand at room temp. for 2 days. The solution was not decolorized and treated as mentioned above, and 1.5 g. of the starting material was recovered.

6-Bromo-7-oxocholesteryl Acetate (IVA)—A mixture of 2 g. of (IIa) and 900 mg. of AcOAg in 30 cc. of glacial AcOH was refluxed for 5 hrs. and filtered. The filtrate was poured into water. The precipitate was collected by filtration, dried, and recrystallized from a mixture of acetone-MeOH to give 500 mg. of silky needles (IVa), m.p. 171~173°C; $\lambda_{\text{max}}^{\text{Nujol}}$ 256 mp (log $\varepsilon$ 4.02); $\nu_{\text{max}}^{\text{Nujol}}$ 1730, 1688, 1595, 1258 cm⁻¹. Anal. Calcd. for C₂₉H₂₉O₂Br: C, 66.78; H, 8.70; Br, 15.32. Found: C, 66.53; H, 8.54; Br, 15.01.

The mother liquor showed the absorption maximum at 295 mp in the U. V. spectrum. Then it was chromatographed over Al₂O₃ and gave 600 mg. of 3α,6,6-bromo-7-oxocholestadiene (V).

6-Bromo-7-oxocholesteryl Benzoate (IVb)—i) AcOAg-AcOH: A mixture of 500 mg. of (IIb) and 200 mg. of AcOAg in 20 cc. of glacial AcOH was refluxed for 5 hrs. Excess of AcOAg and the AgBr formed were filtered off. The filtrate was poured into water, the precipitate was collected by filtration, washed with water, dried, and recrystallized twice from a mixture of CHCl₃-MeOH to give 200 mg. of needles (IVb), m.p. 213~215°C; $\lambda_{\text{max}}$ 230, 240 mp (log $\varepsilon$ 4.22, 4.11); $\nu_{\text{max}}$ 1709, 1695, 1587, 1261 cm⁻¹; $\nu_{\text{max}}^{\text{Nujol}}$ 1712, 1686, 1595 cm⁻¹. Anal. Calcd. for C₂₉H₂₉O₂Br: C, 69.97; H, 8.12; Br, 13.69. Found: C, 70.07; H, 7.92; Br, 13.44.

From the mother liquor 200 mg. of unchanged (IIb) was recovered.

ii) Pyridine: A solution of 5 g. of (IIb) in 17 cc. of pyridine was refluxed for 10 mins. and poured into cold dil. HCl. The precipitate was collected by filtration, washed with a small amount of MeOH and recrystallized twice from a mixture of CHCl₃-MeOH to give 3.5 g. of needles, m.p. 213~215°C, which showed no depression on admixture with the compound obtained above.

Methyl 3a,12a-Diacetoxy-3α,6-bromo-7-oxocholanate (IX)—A solution of 400 mg. of the mixture of (VIII) in 10 cc. of pyridine was refluxed for 10 mins. and poured into cold dil. HCl. The precipitate was collected by filtration, washed with water, dried, and crystallized from MeOH to give crystals (IX), m.p. 210°C (decomp.). Recrystallization from acetone gave 100 mg. of plates (IX), m.p. 220~232°C (decomp.); $\lambda_{\text{max}}^{\text{Nujol}}$ 259 mp (log $\varepsilon$ 3.96); $\nu_{\text{max}}^{\text{Nujol}}$ 1720, 1686, 1590, 1253, 1232 cm⁻¹. Anal. Calcd. for C₂₉H₂₉O₂Br: C, 60.00, H, 6.94; Br, 13.77. Found: C, 59.94; H, 7.34; Br, 13.93.

3α,6-Bromo-7-oxocholestadiene (V)—a) From (IIa): i) A solution of 500 mg. of (IIa) in 5 cc. of collidine was heated at 135°C (oil bath-temp.), diluted with ether, and poured into cold dil. HCl. The ether layer was washed with water, Na₂CO₃ solution, and water, dried over Na₂SO₄, and evaporated to dryness. The residue was recrystallized from acetone to give 200 mg. of needles (V), m.p. 153~155°C. The mother liquor was chromatographed over Al₂O₃ and gave further 50 mg. of needles, m.p. 153~155°C; $\lambda_{\text{max}}^{\text{Nujol}}$ 295 mp (log $\varepsilon$ 4.25); $\lambda_{\text{max}}$ 296 mp (log $\varepsilon$ 4.18); $\nu_{\text{max}}^{\text{Nujol}}$ 1678, 1618, 1585 cm⁻¹; $\nu_{\text{max}}^{\text{Nujol}}$ 1722, 1718, 1558 cm⁻¹; $\nu_{\text{max}}^{\text{Nujol}}$ +28.6 ± 4.6°C (c=0.8334, a=0.238, l=1, CHCl₃). Anal. Calcd. for

12) All melting points are uncorrected. Infrared spectra were measured with a Perkin-Elmer Single-beam Infrared Spectrophotometer, Model 12 C.
C_{25}H_{50}OBr : C, 70.42; H, 8.76; Br, 17.35. Found : C, 70.61; H, 8.71; Br, 17.38.

ii) Refluxing of (IIa) in 10% AgNO₃-pyridine for 10 hrs. or with AcOAg-AcOH for a long time, or treatment with 1% MeOH-KOH at room temp. gave the same compound (V) in each case 50% yield.

b) From (Iva) : Reaction of (Iva) with collidine at 135° for 4 hrs. also gave the above compound (V) in 60% yield.

c) From (Ivb) : Reaction of (Ivb) with collidine at 135° for 6 hrs. also gave the same compound (V) in 55% yield.

d) From (Ivb) : A solution of 1 g. of (Ivb) in 3 cc. of collidine in a sealed tube substituted with CO₂ gas was heated at 185~190°(oil-bath temp.) for 2 hrs. and then added with petr. ether. The collidine hydrobromide formed weighed 100 mg. The petroleum ether solution was washed consecutively with dil. HCl, water, Na₂CO₃, and water, dried over Na₂SO₄, and evaporated to dryness. The residue was crystallized from MeOH to 900 mg. of crystals, m.p. 140~150°, λ<sub>NoH</sub> 295 m.μ. This compound was chromatographed over Al₂O₃. A petr. ether–benzene eluate gave 500 mg. of needles, m.p. 153~155°, and a benzene eluate gave a very small amount of yellow leaflets from MeOH, m.p. 118~120°. The latter compound was negative to Beilstein test. λ<sub>NoH</sub> 230 m.μ(log ε 3.89), 278 m.μ (log ε 4.06), 350 m.μ(log ε 3.62) : v<sub>NoH</sub> 1651, 1628, 1595, 1587 cm<sup>-1</sup>. Anal. Calcd. for C₂₅H₅₀O : C, 85.20; H, 8.59. Found : C, 85.18; H, 10.95.

When the reaction time was prolonged to 8 hrs., the collidine hydrobromide formed weighed 200 mg, but the yield of yellow leaflets was unchanged and the amount of resinous oil increased.

7-Oxocholesteryl Benzoate(VI)—A mixture of 200 mg. of (Ivb) and 2 g. of Zn dust in 10 cc. of EtOH was refluxed for 3 hrs. and filtered off immediately. After cooling, the precipitated crystals were collected by filtration and recrystallized from a mixture of CHCl₃-MeOH to 100 mg. of leaflets (VI), m.p. 162~164°, 180°. Its melting point showed no depression on admixture with the authentic sample and its infrared spectrum was in full agreement with that of the authentic sample. v<sub>NoH</sub> 1715, 1672, 1639, 1456 cm<sup>-1</sup>. Anal. Calcd. for C₁₃₇H₇₈O₃ : C, 80.91; H, 9.58. Found : C, 80.79; H, 9.73.

Δ₄⁻⁷-Oxocholestadiene(III)—A mixture of 500 mg. of (V) and 16 cc. of 5% HBr-AcOH was warmed on a steam bath for 6 hrs. until the mixture turned black, poured into water, and extracted with petr. ether. The extract was washed with Na₂CO₃ and water, dried over Na₂SO₄, and passed through a column of Al₂O₃. An eluate of petr. ether gave a small amount of needles (III), m.p. 110~112° from MeOH. Its melting point showed no depression on admixture with the authentic sample and its infrared spectrum was in full agreement with that of the authentic sample. λ<sub>NoH</sub> 277 m.μ; v<sub>NoH</sub> 1655, 1628, 1596 cm<sup>-1</sup>, v<sub>CHCl</sub> 1653, 1626, 1596 cm<sup>-1</sup>. Anal. Calcd. for C₂₇H₄₆O : C, 84.76; H, 11.06. Found : C, 84.69; H, 11.37.

Summary

(1) It has been demonstrated that dibromination of 7-oxocholesteryl acetate or benzoate gives corresponding 6,6-gem-dibromide.

(2) The structure of these dibromides was determined by characteristics absorptions in the ultraviolet and infrared spectra and from the results of some chemical reactions.

(3) Dibromination of methyl 13α,12α-diacehtoxy-7-oxocholanolate was also examined.

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