EXPERIMENTAL
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All melting points are uncorrected. I.r. spectra were determined in KBr with a Perkin-Elmer 237 Spectrophotometer. N.m.r. spectra were run in CDCl$_3$ on a Varian A60 or HA 100 spectrometer with TMS as internal standard. U.v. spectra were determined in 95% ethanol with a Beckman DB spectrophotometer. Mass spectra were measured in an AEI MS-9 mass spectrometer using a direct insertion sample inlet system. Rotations were determined in CHCl$_3$. Thin layer chromatographic plates were prepared from silica gel G and sprayed with aqueous perchloric acid (20%). Light petroleum refers to a fraction of b.p. 60-80°C. N.m.r. values are given in ppm (s=singlet, d=doublet, t=triplet, br=broad, umc=unresolved multiplet centred at, mc=multiplet centred at). I.r. values are given in cm$^{-1}$ (s=strong, m=medium, br=broad, sh=shoulder, w=weak).

3β-Acetoxycholest-5-ene (CCXXVII)

A mixture of cholesterol (100 g), pyridine (150 ml) and freshly distilled acetic anhydride (100 ml) was heated on a water bath for 2 hours. A brown solution was obtained which after allowing to cool at room temperature was poured into crushed ice-water mixture with stirring. A white precipitate thus obtained was filtered under suction, washed with water and air dried. The crude acetate was recrystallized from acetone (97 g), m.p. 114-15°C (Lit. 179 m.p. 116°C).
3\(\beta\)-Acetoxy-5,6-secocholestan-5-keto-6-oic acid (XCVIII)

To a well stirred mixture of 3\(\beta\)-acetoxycholesterol-5-ene (CCXXVII) (54 g) and glacial acetic acid (600 ml), a solution of chromium trioxide (35 g) in 50% acetic acid (100 ml) was added over a period of 2 hours and the mixture was maintained at 55-60° throughout. After complete addition, the mixture was stirred for additional 2 hours at the same temperature. The excess of chromic acid was destroyed by the addition of methanol (30 ml) and then acetic acid (400 ml) was removed by distillation under reduced pressure. The remaining liquid was diluted with water (25 ml) and allowed to stand in the cold for 12 hours. The crystalline 3\(\beta\)-acetoxycholesterol-5-en-7-one (LXXVIII) separated as plates was removed by filtration under suction and washed with acetic acid (80\%, 50 ml) (16 g), m.p. 152-155°. Several recrystallizations from methanol raised the m.p. to 161-163° (Lit.\(^46\) m.p. 164°); \(\nu_{\text{max}}\) 1734s (CH\(_3\)COO), 1680s (C=C-C=O), 1630m (C=C-C=O), 1235s cm\(^{-1}\) (acetate); \(\delta(100\ \text{MHz})\) 5.65s (1 proton, C\(_6\)-H), 4.7br (1 proton, C\(_3\)-\(-\text{H}\)), 2.0s (3 protons, CH\(_3\)COO), 1.08s (3 protons, C\(_{12}\)-CH\(_3\)), 0.65s (3 protons, C\(_{13}\)-CH\(_3\)), 0.78, 0.82, 0.89 (other methyl protons); M\(^+\) 442 (C\(_{29}\)H\(_{46}\)O\(_3\)).

The filtrate was diluted with 50% methanol-water (70 ml), seeded with a sample of the seco acid (XCVIII) and placed in a refrigerator for a period of 10-12 days. The seco acid
which crystallized out as a thick green coloured mass was filtered under suction and washed with 75% acetic acid (100 ml). The crude material (13 g) melted at 116-119°. The recrystallized sample of the seco acid (XCVIII) from methanol had m.p. 128-130°; $\left\{\frac{\alpha}{\alpha}\right\}_D^{20} + 77.5^\circ$ (Lit. $^{179,180} \left\{\frac{\alpha}{\alpha}\right\}_D^{20} + 77.9^\circ$; m.p. 127-129°). (Found: C, 73.32; H, 10.42. Calcd. for $\text{C}_{29}\text{H}_{48}\text{O}_5$ C, 73.07; H, 10.15%). $\gamma_{\max}$ 3350-3200 br (COOH), 1738 s (CH$_3$COO), 1712 s (COOH), 1240 s cm$^{-1}$ (acetate); $\delta$(100 MHz), 9.8 s (1 proton, disappeared on addition of D$_2$O, COOH), 5.3 br (1 proton, C$_3$H$_2$), 2.0 s (3 protons, CH$_3$COO), 1.01 s (3 protons, C$_{10}$H$_7$), 0.7 s (3 protons, C$_{13}$H$_7$), 0.82, 0.91 (other methyl protons).

Note: The isolation of the seco acid (XCVIII) in the crystalline form often failed and therefore, attempts were made to isolate the seco acid (XCVIII) by alkali extraction procedure followed by purification by column chromatography over silica gel. In each case the product obtained was a noncrystallizable oil having similar $R_f$ value as that of the seco acid (XCVIII). The product was identified as the $\alpha,\beta$-unsaturated seco acid (CCLXXXVIII). It appears that during alkaline extraction and column chromatography, elements of acetic acid are eliminated.
Methyl 3β-acetoxy-5-keto-5,6-secocholestan-6-oate (CCCXVI)

The seco acid (XCVIII) (1 g) in ether (20 ml) was treated with an excess of an ethereal solution of diazomethane in the cold. The reaction mixture was allowed to stand in the cold for 30 minutes and the excess of diazomethane decomposed by the addition of dilute acetic acid. The ethereal solution was washed with water, sodium bicarbonate solution (5%) and water and dried over anhydrous sodium sulphate. Removal of the desiccant and the solvent provided an oil which was crystallized from methanol in the cold (0.96 g), m.p. 81-82 °; $\gamma_{\text{max}}^{20} + 64.5^\circ$ (Lit. 79.2-80.6 °; $\gamma_{\text{max}}^{20} + 64.7^\circ$); $\delta(100 \text{ MHz})$ 5.3 br (1 proton, $\text{C}_3$-H), 3.55 s (3 protons, COOCH$_3$), 2.01 s (3 protons, CH$_3$COO), 1.01 s (3 protons, C$_{10}$-CH$_3$), 0.7 s (3 protons, C$_{13}$-CH$_3$), 0.92, 0.91 (other methyl protons).

3β-Acetoxy-6-oxa-B-homocholestan-4-en-7-one (XCIX)

(i) Reaction of the seco acid (XCVIII) with acetic anhydride-sodium acetate

The seco acid (XCVIII) (1 g) was heated under reflux with acetic anhydride (60 ml, freshly distilled) for 2 hours. The reaction mixture was allowed to attain room temperature
and freshly fused sodium acetate (ca 60 mg) was added and the heating continued for additional 4 hours. The acetic anhydride was removed by distillation under reduced pressure and the residue dissolved in ether. The ethereal extract was washed with water, sodium bicarbonate solution (5%) and water and dried over anhydrous sodium sulphate. Removal of the desiccant and the solvent gave an oil (ca 1 g) which was found to be composed of 2 components by t.l.c. It was chromatographed over silica gel (20 g; NCL grade). Each fraction of 20 ml was collected. Elution with light petroleum provided B-norcholesta-3,5-diene (CCXIII), crystallized from ethanol (130 mg), m.p. 76° (Lit. 174 m.p. 76.5-77°); red colour with tetranitromethane; ν max 1640m cm⁻¹ (C=C-C=C); δ (60 MHz) 5.37-6.37br, m (3 protons, C₃-H, C₄-H and C₆-H - vinylic protons), 0.92s (3 protons, C₁₀-CH₃), 0.7s (3 protons, C₁₃-CH₃), 0.86, 0.82 (other methyl protons).

Elution with light petroleum-ether (10:1) gave the enol lactone (XCIX)(400 mg)(homogeneous by t.l.c.) as a non-crystallizable glassy solid giving no reproducible melting point. (Found: C, 75.70; H, 9.82. C₂₉H₄₆O₄ requires C, 75.98; H, 10.04%); ν max 1770s (C=O-CH₃, enol lactone carbonyl), 1750s (CH₃COO), 1670m (C=O), 1240s cm⁻¹ (acetate); δ (100 MHz) 5.2-5.6br (2 protons, AcO-C-H and C₄-H, vinylic proton), 2.4d like (2 protons, C₇a-H₂), 2.03s (3 protons, CH₃COO), 1.13s (3 protons, C₁₀-CH₃), 0.7s (3 protons, C₁₃-CH₃), 1.0, 0.92, 0.83 (other methyl protons); M⁺ 458 (C₂₉H₄₆O₄).
Reaction of the seco acid (XCVIII) with acetic anhydride-acetyl chloride

The seco acid (XCVIII) (1 g) was heated under reflux with acetic anhydride (6 ml) and acetyl chloride (0.2 ml) for 4 hours. The acetic anhydride was removed under reduced pressure and the residue was taken up in ether. The ethereal solution was washed with water, sodium bicarbonate solution (5%) and water and dried over anhydrous sodium sulphate. After usual work up of the ethereal solution, an oil was obtained which was treated with a small amount of methanol to destroy the last traces of the acetic anhydride. The resultant oily product (ca 1 g, t.l.c. indicated the presence of two components) was chromatographed over silica gel (20 g; NCL grade) and eluted in 20 ml fractions. Elution with light petroleum gave the diene (CCXCLIII), which was crystallized from ethanol (135 mg), m.p. and m.m.p. 76° (Lit. 174 m.p. 76.5-77°).

Elution with light petroleum-ether (10:1) gave the enol lactone (XCIX) (410 mg) which was characterized by comparison with the sample obtained in the previous experiment (i.r., n.m.r. and t.l.c. identical).
Methanolation of the enol lactone (XCIX): Methyl 5-keto-5, 6-secocholest-3-en-6-oate (CCLXXXIX).

The enol lactone (XCIX) (100 mg) was mixed with a solution of sodium methoxide in methanol (prepared by dissolving a small piece of freshly cut sodium metal in 15 ml of absolute methanol) and the reaction mixture allowed to stand at room temperature for 12 hours. It was diluted with an excess of water, acidified with HCl and extracted with ether. The ethereal solution was washed with water and dried over anhydrous sodium sulphate. Removal of the desiccant and the solvent afforded the methyl ester (CCLXXXIX) as a non crystallizable oil (ca 60 mg); \( \lambda_{\text{max}} \) 230 nm (log \( \varepsilon \) 4.04); \( \nu_{\text{max}} \) 3040w (C=H), 1742s (COOCH\(_3\)), 1685s cm\(^{-1}\) (C=C-O=O); \( \delta \) (60 MHz) 6.7m (1 proton, C\(_3\)-H, \( \beta \) to carbonyl group), 5.78d (J=11 Hz, 1 proton, C\(_4\)-H), 3.57s (3 protons, COOCH\(_3\)), 2.3d like (2 protons, CH\(_2\)COOCH\(_3\)), 1.1s (3 protons, C\(_{10}\)-CH\(_3\)), 0.68s (3 protons, C\(_{13}\)-CH\(_3\)), 0.82, 0.9 (other methyl protons); M\(^+\) 430 (C\(_{29}\)H\(_{46}\)O\(_3\)). This compound was found to be identical (u.v., i.r., n.m.r., mass, t.l.c.) with an authentic sample of (CCLXXXIX) prepared according to literature procedure\(^{170}\).

5-Keto-5,6-secocholest-3-en-6-oio acid (CCLXXXVIII)

The seco acid (XCVIII) (1 g) was dissolved in methanol (100 ml) and to this, sodium bicarbonate (1 g) was added.
The reaction mixture was allowed to stand at room temperature for 27 hours with occasional shaking. Towards the end of the reaction period, most of the added bicarbonate had gone into the solution. The reaction mixture was diluted with water (300 ml), acidified (HCl) and extracted with ether. The ethereal solution was washed with water and dried over anhydrous sodium sulphate. It provided the acid (CCLXXXVIII) (0.87 g) as a non crystallizable oil; $\lambda_{\text{max}}$ 232 nm ($\log \epsilon$ 4.0); $\gamma_{\text{max}}$ 3400-3200 br (COOH), 1710 s (COOH), 1685 s cm$^{-1}$ (C=C-C=O).

Methyl 5-keto-5,6-secocholest-3-en-6-oate (CCLXXXIX)

A solution of the seco acid (CCLXXXVIII) (1 g) in the cold ether (20 ml) was treated with an excess of an ethereal solution of diazomethane. After usual work up of the reaction mixture, the methyl ester (CCLXXXIX) (0.8 g) was obtained as a homogeneous oil. The spectral values of this compound have been reported earlier and are the same as obtained for the methanolysis product of the enol lactone (XCIX).

3β-Acetoxy-6-nitrocholest-5-ene

3β-Acetoxycholest-5-ene (CCXXVII) (5 g) was covered with nitric acid (sp.gr., 1.52, 125 ml) and sodium nitrite
(5 g) was gradually added over a period of 1 hour with continuous stirring. Slight cooling was also affected during the course of the reaction and stirring was continued for additional 2 hours when a yellow spongy mass separated on the surface of the mixture. The mixture was diluted with cold water (100 ml) when a green coloured mass was obtained. The whole mass was extracted with ether and the ethereal solution washed with water, sodium bicarbonate solution (5%) (until the washings were pink) and water and dried over anhydrous sodium sulphate. Removal of the desiccant and the solvent provided the desired nitro compound as an oil, which crystallized from methanol containing traces of acetone (3.5 g), m.p. 104° (Lit. \textsuperscript{181} m.p. 102-104°); \( \delta_{\text{max}} \) 1740s (CH\textsubscript{3}COO), 1515m (C-C-NO\textsubscript{2}), 1233s cm\textsuperscript{-1} (acetate); M\textsuperscript{+} was not observed. Highest mass peak was observed at m/e 413 (C\textsubscript{27}H\textsubscript{43}NO\textsubscript{2}; M\textsuperscript{+} - CH\textsubscript{3}COOH).

3\textbeta-Acetoxy-5\textbeta-cholestan-6-one (XXVII)

3\textbeta-Acetoxy-6-nitrocholest-5-ene (3 g) was dissolved in warm acetic acid (125 ml). Zinc dust (6 g) was added in small portions with shaking. The suspension was heated under reflux for 4 hours and water (6 ml) was added now and then during the course of the reaction. The hot solution was filtered, cooled to room temperature and diluted with an excess of ice cold water. The precipitate thus obtained was
extracted with ether and the ethereal solution washed with water, sodium bicarbonate solution (10%) and water and dried over anhydrous sodium sulphate. Evaporation of the solvent gave the desired ketone (XXVII) as an oil which crystallized from methanol (2.1 g), m.p. 128-129° (Lit. 182 m.p. 127-128°).

### 3β-Acetoxy-5α-bromocholestan-6-one

To a cooled solution of 3β-acetoxy-5α-cholestan-6-one (XXVII) (2 g) in ether (20 ml) and acetic acid (5 ml), bromine solution (1.1 g of bromine in 15 ml of acetic acid) was added gradually. Few drops of HBr (48%) was added to catalyse the reaction. The desired bromoketone started crystallizing out from the reaction mixture when about half of the bromine solution was added. The bromo ketone was filtered and recrystallized from chloroform-ether mixture (1.2 g), m.p. 162-164° (Lit. 183 m.p. 162°); ν_max 1735s (CH_3-CO-O), 1720s cm⁻¹ (CO); δ (100 MHz) 5.35br (1 proton, C_3-CH-H), 2.3d (2 protons, C_7-H_2), 2.03s (3 protons, CH_3-COO), 1.0s (3 protons, C_10-CH_3), 0.7s (3 protons, C_13-CH_3), 0.92, 0.83 (other methyl protons).

### 3β-Acetoxycholest-4-en-6-one (CLXVII)

A solution of 3β-acetoxy-5α-bromocholestan-6-one (2 g) in pyridine (20 ml, freshly distilled over solid KOH)
was heated under reflux for 8 hours under anhydrous conditions. The reaction mixture was poured into ice cold water, acidified (HCl) and extracted with ether. The ethereal layer was washed successively with water, dilute HCl, water, sodium bicarbonate solution (5%) and water and dried over anhydrous sodium sulphate. Removal of the solvent gave an oil which crystallized from methanol to give the ketone (CLXVII) (1.3 g), m.p. 108-110° (Lit. 183 m.p. 110°); M* 442 (C_{29}H_{46}O_{3}).

**Attempted Baeyer-Villiger Oxidation of 3β-acetoxycholest-4-en-6-one (CLXVII)**

To a solution of the ketone (CLXVII) (2 g) in chloroform (10 ml), a chloroform solution of perbenzoic acid (1 to 2.5 mole equiv.) and a few crystals of p-toluenesulphonic acid was added and the reaction mixture allowed to stand at room temperature for 96 hours. The progress of the reaction was monitored by t.l.c. The reaction mixture was poured into ice cooled water and extracted with ether. The ethereal layer was washed with sodium bicarbonate solution (5%) and water and dried over anhydrous sodium sulphate. Removal of the solvent gave an oil (ca 1.9 g). T.l.c. of the crude product, in each case, indicated the presence of several components and none of the components was comparable with the enol lactone (XCIX).
3β-Chlorocholest-5-ene

Freshly purified thionyl chloride (75 ml) was added to cholesterol (100 g) at room temperature. A vigorous reaction ensued with the evolution of gaseous products. When the reaction slackened, the mixture was gently heated at a temperature of 55-60° on a water bath for 30 minutes and then poured into cold water with stirring. The yellow solid thus obtained was filtered under suction, washed thoroughly with cold water and air dried. Recrystallization from acetone gave 3β-chlorocholest-5-ene (94 g), m.p. 96-97° (Lit. m.p. 96-97°)(positive Beilstein test and yellow colour with tetranitromethane); $\nu_{\text{max}}$ 1640 w (C=C), 715 m cm$^{-1}$ (C-Cl); $\delta$ (100 MHz) 5.32 m (1 proton, $C_6$-H, vinylic proton), 3.7 br (1 proton, $W_2^1 = 18$ Hz, $C_3\alpha$-H, axial proton)$^{175}$, 1.02 s (3 protons, $C_{10}$-CH$_3$), 0.67 s (3 protons, $C_{13}$-CH$_3$), 0.82, 0.89, 0.91 (other methyl protons); M$^+$ 404/406 (3:1) (C$_{27}$H$_{45}$Cl).

Cholest-5-ene (CCXCV)

3β-Chlorocholest-5-ene (10 g) was dissolved in warm amyl alcohol (230 ml) and sodium metal (20 g) was added to the solution with continuous stirring over a period of 8 hours. The reaction mixture was warmed occasionally. When all the sodium had dissolved, the reaction mixture was poured into dilute hydrochloric acid and the acidified solution allowed
to stand over night at room temperature. A white crystalline solid thus obtained was filtered under suction, washed thoroughly with water and air-dried. The crude product was recrystallized from acetone to furnish cholest-5-ene (8.3 g), m.p. 94°C (Lit. 89-91°C); ʋmax 1640 w cm⁻¹ (C=C); δ (60 MHz) 5.22m (1 proton, C6-H, vinylic proton), 0.94s (3 protons, C10-CH3), 0.68s (3 protons, C14-CH3), 0.83, 0.9 (other methyl protons); M⁺ 370 (C27H46).

Chromic acid oxidation of cholest-5-ene: 5-Keto-5,6-secocholestan-6-oic acid (CVII) and cholest-5-en-7-one (LXXXIII)

Cholest-5-ene (13 g) was dissolved in warm acetic acid (700 ml) and to this a solution of chromium trioxide (16 g) in 50% acetic acid (50 ml) was added with continuous stirring over a period of 2 hours. After the complete addition of chromic acid solution, the reaction mixture was stirred at 70-75°C for additional 2 hours. The excess of chromic acid was destroyed by addition of methanol (20 ml). The bulk of the acetic acid was removed by distillation under reduced pressure when a green viscous material was obtained. It was extracted with ether (3 x 150 ml) and the ethereal solution was washed with water and then extracted with sodium hydroxide solution (10%, 4 x 50 ml). The ether solution was washed with water and dried over anhydrous sodium sulphate. Removal of the desiccant and the solvent provided cholest-5-en-7-one
which was purified by column chromatography over silica gel (60 g; NCL grade)(2.5 g), m.p. 127-130° (Lit. 185 m.p. 125-129°); \( \nu_{\text{max}} \) 1688 s cm\(^{-1} \) (C=C-C=O).

The combined alkaline extract was acidified with hydrochloric acid and the liberated organic acid was extracted with ether. The ethereal solution was washed with water and dried over anhydrous sodium sulphate. After usual work up of the ether solution an oil (ca 5 g) was obtained. This was purified by column chromatography over silica gel (100 g; NCL grade). The purified acid (CVII) was obtained as a viscous oil\(^{55} \) (3.5 g)(homogeneous by t.l.c.); \( \nu_{\text{max}} \) 3400-3200 br (COOH), 1715 s, 1705 s cm\(^{-1} \) (C=O, COOH); \( \delta \) (60 MHz) 10.6s (1 proton, disappeared on addition of D\(_2\)O, COOH), 2.3 umc (4 protons, COCH\(_2\) and CH\(_2\)COOH), 1.0s (3 protons, C\(_{10}\)-CH\(_3\)), 0.7s (3 protons, C\(_{13}\)-CH\(_3\)), 0.82, 0.90 (other methyl protons); M\(^+\) 418 (C\(_{27}\)H\(_{46}\)O\(_3\)).

**Methyl 5-keto-5,6-secocholestan-6-oate (CX)**

The seco acid (CVII)(500 mg) was dissolved in ether and the solution cooled in an ice bath. To this, excess of an ethereal solution of diazomethane was added till a yellow colour persisted. The reaction mixture was kept in the cold for 15 minutes and the excess of diazomethane decomposed by dilute acetic acid. The ethereal solution was washed with
water, sodium bicarbonate solution (5%) and water and dried over anhydrous sodium sulphate. Removal of the solvent provided the desired methyl ester (C3), which crystallized from methanol in the cold (400 mg), m.p. 102-103° (Lit. 55 m.p. 102-103°); $\delta_{\text{max}}$ 1735 s (COOCH₃), 1708 s cm⁻¹ (C=O); $\delta$ (100 MHz) 3.56 s (3 protons, COOCH₃), 2.2 umc (4 protons, COCH₂ and CH₂COOCH₃), 1.0 s (3 protons, C₁₀-CH₃), 0.68 s (3 protons, C₁₃-CH₃), 0.83, 0.9 (other methyl protons); M⁺ 432 (C₂₈H₄₈O₃).

6-Oxa-3-homocholest-4-en-7-one (CXIII)

(i) Reaction of the seco acid (CVII) with acetic anhydride–sodium acetate

The seco acid (CVII) (1 g) and acetic anhydride (45 ml, freshly distilled) were mixed together and the mixture heated for 2 hours under reflux. It was allowed to attain room temperature and freshly fused sodium acetate (ca 70 mg) was added and the heating continued for additional 4 hours. The acetic anhydride was removed by distillation under reduced pressure and the residue taken up in ether. The ethereal solution was washed with water, sodium bicarbonate solution (5%) and water and dried over anhydrous sodium sulphate. Removal of the solvent gave an oil which was warmed with a small amount of methyl alcohol to destroy the remaining traces.
of acetic anhydride. The resultant oil (ca 1 g) showed the presence of 2 components by t.l.c. It was chromatographed over silica gel (20 g; NCL grade). Each fraction of 20 ml was collected. Eluates from light petroleum gave 8-norcholest-5-ene (CIX), which crystallized from methanol (150 mg), m.p. and m.m.p. $17^\text{1} 68^\circ$, positive tetranitromethane test; $\gamma_{\text{max}}$ 3030w (C=C-H), 1625w cm$^{-1}$ (C=C); $\delta$ (60 MHz) 5.28d like (1 proton, C$_6$-H, vinylic proton), 1.0s (3 protons, C$_{10}$-CH$_3$), 0.68s (3 protons, C$_{13}$-CH$_3$), 0.93, 0.82 (other methyl protons); M$^+$ 356 (C$_{26}$H$_{44}$).

Elution with light petroleum–ether (10:1) provided the enol lactone (CXIII), which crystallized from light petroleum (380 mg), m.p. 93-94$^0$ (Found: C, 80.77; H, 10.82. C$_{27}$H$_{44}$O$_2$ requires C, 81.0; H, 11.0%); $\gamma_{\text{max}}$ 1772s (C=O–C=O, enol lactone carbonyl), 1668s cm$^{-1}$ (C=O); $\delta$ (60 MHz) 5.53t (1 proton, C$_4$–H, vinylic proton), 2.4 umc (4 protons, C$_3$–H$_2$ allylic to C$_4$–C$_5$ double bond, and C$_7$–H$_2$), 1.0s (3 protons, C$_{10}$-CH$_3$), 0.73s (3 protons, C$_{13}$-CH$_3$), 0.93, 0.83 (other methyl protons); M$^+$ 400 (C$_{27}$H$_{44}$O$_2$).

(ii) Reaction of the seco acid (CVII) with acetic anhydride–acetyl chloride

A mixture of the seco acid (1 g), acetic anhydride (6 ml, freshly distilled) and acetyl chloride (ca 0.2 ml) was heated under reflux for 4 hours. The excess of the acetic
anhydride was removed by distillation under reduced pressure and the residue worked up in the manner previously described for (XCVIII). Column chromatography of the crude product gave B-norcholest-5-ene (CIX) (135 mg), m.p. and m.m.p. 68-69° and the enol lactone (CXIII) (390 mg), m.p. and m.m.p. 93-94°.

**Methanolysis of the enol lactone (CXIII):Methyl 5-keto-5, 6-secocholestan-6-oate (CX).**

The enol lactone (CXIII) (60 mg) was treated with sodium methoxide in absolute methanol and the reaction mixture kept at room temperature for 12 hours. It was worked up in the manner described for (XCIX) to give the methyl ester (CX) (50 mg). The crude product was purified by column chromatography over silica gel (5 g; NCL grade). Each fraction of 15 ml was collected. Elution with light petroleum-ether (5:1) gave the pure methyl ester (CX) (35 mg), m.p. and m.m.p. 102-103°. It was found to be identical in all other respects with the methyl ester obtained by methylation (diazomethane) of the seco acid (CVII).

**6-Nitrocholest-5-ene**

A suspension of finely powdered cholest-5-ene (CCXCIV) (3 g) in glacial acetic acid was stirred at room temperature for 5 minutes. Fuming nitric acid (sp.gr. 1.5, 10 ml) was
rapidly added and the stirring continued for 2 hours. The temperature of the reaction mixture was maintained between 20-25° by external cooling. The reaction was then diluted with cold water when a yellow solid separated. It was collected by filtration under suction, washed with water and air-dried. Recrystallization from methanol furnished the desired compound (1.6 g), m.p. 117-118° (Lit. 186 m.p. 117-118°); \( \gamma_{\text{max}} \) 1640w (C=C), 1505m cm\(^{-1}\) (C=C-NO\(_2\)); \( M^+ \) 415 (C\(_{27}\)H\(_{45}\)NO\(_2\)).

\( 5\alpha \)-Cholestan-6-one (XXVI)

6-Nitrocholest-5-one (3 g) was dissolved in warm glacial acetic acid (100 ml) and to this, zinc dust (6 g) was added in small portions. The suspension was heated under reflux for 3 hours and 12 ml of water was added now and then during the course of the reaction. The solution was filtered and the residue washed with warm acetic acid (2 x 10 ml). The filtrate was diluted with water till a turbidity developed and the mixture was allowed to stand at room temperature for 24 hours. The crystalline material thus separated was filtered under suction and washed thoroughly with water. Recrystallization from ethanol gave the desired ketone (XXVI) (1.8 g), m.p. 97-98° (Lit. 187 m.p. 95-96°); \( \gamma_{\text{max}} \) 1705s cm\(^{-1}\) (C=O); \( M^+ \) 386 (C\(_{27}\)H\(_{46}\)O).
5\textcircled{\textprime}\textendash bromocholestan\textendash 6\textendash one

A solution of 5\textcircled{\textprime}\textendash cholestan\textendash 6\textendash one (XXVI) (6 g) in acetic acid (18 ml) and ether (90 ml) was cooled in an ice bath. Bromine solution (4.1 g of bromine in 58 ml of acetic acid) was added dropwise to the cooled solution of the ketone (XXVI). Few drops of HBr (48\%\) was added to catalyse the reaction. After the complete addition of the bromine solution, the desired bromo ketone, which precipitated out, was filtered under suction and recrystallized from chloroform\textendash ether mixture (3.6 g), m.p. 102° (Lit.\textsuperscript{190} m.p. 102°).

Cholest-4\textendash en-6\textendash one (CXL\textendash I)

A mixture of 5\textendash \textcircled{\textprime}\textendash bromocholestan\textendash 6\textendash one (3 g) and pyridine (30 ml, freshly distilled) was heated under reflux for 8 hours under anhydrous conditions. The reaction mixture was poured into cold water, acidified with hydrochloric acid and extracted with ether. Usual work up of the ethereal solution gave the ketone (CXL\textendash I), which was crystallized from methanol (2.1 g), m.p. 107\textendash 109° (Lit.\textsuperscript{179} m.p. 108\textendash 109°).

Attempted Baeyer\textendash Villiger oxidation of cholest-4\textendash en-6\textendash one (CXL\textendash I)

To a solution of the ketone (CXL\textendash I) (2 g) in chloroform (20 ml), a chloroform solution of perbenzoic acid (1 to 2.5 mole equiv.) was added. The reaction was catalysed by a few crystals
of p-toluenesulphonic acid. The reaction mixture was kept at
room temperature for 96 hours. The progress of the reaction was
pursued by t.l.c. It was poured into ice cold water and worked up in the manner described for (CLXVII). An oily product
thus obtained was found to be a mixture of several components (t.l.c.). Only one of the products appeared to be the desired enol lactone (CXIII), the isolation of which by conventional column chromatography did not prove to be encouraging.

6-Oxa-B-homocholesta-2,4-dien-7-one (CCXC)

(1) Reaction of the seco acid, 5-keto-5,6-secocholesta-
3-en-6-oic acid (CCLXXXVIII) with acetic anhydride-
sodium acetate

The seco acid (CCLXXXVIII)(1 g) was heated under reflux with acetic anhydride (60 ml, freshly distilled) for 2 hours. After allowing the reaction mixture to attain room temperature, freshly fused sodium acetate (ca 60 mg) was added and the heating continued for additional 4 hours. The acetic anhydride was removed by distillation under reduced pressure and the residue worked up in the usual manner. It provided an oil (ca 1 g) which was found to be a mixture of 2 components (t.l.c.). The oil was subjected to column chromatography over silica gel (20 g; NCL grade). Each fraction of 20 ml was collected. Elution with light petroleum
provided B-norcholesta-3,5-diene (CCXCIII), which crystallized from ethanol (150 mg), m.p. and m.m.p. 76°C (Lit. 174 m.p. 76.5-77°C).

Elution with light petroleum-ether (10:1) gave the dienol lactone (CCXC) as an oil (300 mg, homogeneous by t.l.c.).

(Found: C, 81.2; H, 10.6. C27H42O2 requires C, 81.4; H, 10.55%);

$\lambda_{max}$ 270 nm (log ε 4.01); $\gamma_{max}$ 1766s (C=C=C=O-C=O, dienol lactone carbonyl), 1665s (C=C-O), 1650m cm$^{-1}$ (C=C); δ (60 MHz) 5.4-6.1br,m (3 protons, C$_2$-H, C$_3$-H, and C$_4$-H, vinylic protons), 2.4m (4 protons, C$_1$-H$_2$, allylic methylene and C$_7$-H$_2$, α-methylene to a carbonyl group), 1.05s (3 protons, C$_{10}$-CH$_3$), 0.7s (3 protons, C$_{13}$-CH$_3$), 0.91, 0.8 (other methyl protons); M$^+$ 398 (C$_{27}$H$_{42}$O$_2$).

(ii) Reaction of the seco acid (CCLXXXVIII) with acetic anhydride-acetyl chloride

A mixture of the seco acid (CCLXXXVIII)(1 g), acetic anhydride (6 ml, freshly distilled) and acetyl chloride (ca 0.2 ml) was heated under reflux for 4 hours. The excess of the acetic anhydride was removed by distillation under reduced pressure and the residue worked up in the manner described for (XCVIII). The column chromatography of the crude product gave B-norcholesta-3,5-diene (CCXCIII)(150 mg), m.p. and m.m.p. 76°C and the dienol lactone (CCXC) as an oil, which was found to be identical with a sample of (CCXC) obtained in the preceding experiment.
Methanolysis of the dienol lactone (CCXC): Methyl 5-keto-5,
6-secocholest-2-en-6-oate (CCXCV)

The dienol lactone (CCXC) (100 mg) was treated with
sodium methoxide in methanol and the reaction mixture kept at
room temperature for 12 hours. It was diluted with water,
acidified (HCl) and extracted with ether. After usual work
up of the ethereal extract, an oil (ca 100 mg) was obtained
which was chromatographed over silica gel (5 g; NCL grade).
Each fraction of 10 ml was collected. Eluates from light
petroleum-ether (10:1) gave the methyl ester (CCXCV) (60 mg,
homogeneous by t.l.c.). (Found: C, 78.0; H, 10.52. C_{28}H_{46}O_{3}
requires C, 78.14; H, 10.69%); \( \nu_{\text{max}} \) 3035w (C=H), 1740s
(COOCH_{3}), 1708s (C=O), 1636w (C=C); U.v. spectrum was feature­
less in the region 220-360 nm., \( \delta \) (60 MHz), 5.6mc (2 protons,
C_{2}-H and C_{3}-H, vinylic protons), 3.6s (3 protons, COOCH_{3}),
2.35 umc (6 protons, C_{1}-H_{2}, C_{4}-H_{2} and C_{7}-H_{2}), 1.0s (3 protons,
C_{10}-CH_{3}), 0.68s (C_{13}-CH_{3}), 0.9, 0.82 (other methyl protons);
M^{+} 430 (C_{28}H_{46}O_{3}).

Acid-catalysed isomerization of (CCXCV) to (CCLXXXIX)

The methyl ester (CCXCV) (100 mg) was dissolved in
absolute methanol (30 ml) and to this a few drops of conc.
sulphuric acid was added and the mixture heated under reflux
for 1 hour. The reaction mixture was then poured into ice
cooled water and extracted with ether. The ethereal solution was washed thoroughly with water and dried over anhydrous sodium sulphate. Removal of the desiccant and the solvent gave an oil which was treated with diazomethane in ether. Usual work up of the reaction mixture followed by column chromatography over silica gel gave (CCLXXXIX) (ca 55 mg), which was found to be identical with an authentic sample of (CCLXXXIX) in all respects.

5α- and 5β-Chlorocholestanes

Cholest-5-ene (CCXCVI) (2 g) was dissolved in chloroform (80 ml) and dry hydrogen chloride gas was passed slowly through the solution for 4 hours at room temperature. The solution was kept overnight and the chloroform was removed by distillation under reduced pressure. The oily residue was crystallized from acetone to give a mixture of 5α- and 5β-chlorocholestanes (1.3 g), m.p. 96° (Lit. 188 m.p. 97°).

In one or two experiments, a compound, m.p. 121° was also obtained along with 5α- and 5β-chlorocholestanes. This was identified as 5α,6β-dichlorocholestane by elemental analysis, spectral properties and its conversion to cholest-5-ene. (Found: C, 73.60; H, 10.5. Calcd. for C27H46Cl2
C, 73.63; H, 10.45%; δ (60 MHz) 4.33d,d (1 proton, C6-H,
J C6-H, C7β-H = 2.5 Hz, J C6α-H, C7α-H = 5 Hz), 1.32s (3 protons, C10-CH3), 0.73s (3 protons, C13-CH3), 0.95, 0.90, 0.82 (other methyl protons).)
Treatment of the dichloro compound, m.p. 121° with zinc dust

5α,6β-Dichlorocholestanee (1 g) was dissolved in a mixture of ether (25 ml) and acetic acid (5 ml) and to the resultant solution, zinc dust (2 g) was added in small portions over a period of 10 minutes with shaking. The reaction mixture was allowed to stand at room temperature for 1 hour with frequent shaking. Zinc dust was removed by filtration and the filtrate washed with water, sodium bicarbonate solution (5%) and water and dried over anhydrous sodium sulphate. Removal of the desiccant and the solvent provided cholest-5-ene (0.8 g), m.p. and m.m.p. 93-95°.

5α,6β-Dichlorocholestanee

Through a solution of cholest-5-ene (1 g) in chloroform (60 ml), dry chlorine gas was passed for about 2 hours and the reaction mixture kept overnight at room temperature. The solvent was removed by distillation under reduced pressure and the residue crystallized from acetone-ether mixture to give 5α,6β-dichlorocholestanee (0.31 g), m.p. and m.m.p. 121°.

Cholest-4-ene

A solution of 5α- and 5β-chlorocholestanees (2 g) in pyridine (20 ml) was heated under reflux for 7 hours. The reaction mixture was cooled, diluted with cold water and
extracted with ether. The ethereal extract was washed successively with water, dilute hydrochloric acid, water, sodium bicarbonate solution (5%) and water and dried over anhydrous sodium sulphate. Removal of the solvent gave cholest-4-ene which was crystallized from methanol-ether mixture (1.3 g), m.p. 80-82° (Lit. 179 m.p. 83°); \( \gamma_{\text{max}} \) 3020\( \text{cm}^{-1} \) (C=C); \( \delta(60 \text{MHz}) \) 5.22m (1 proton, C\(_4\)-H, vinylic proton), 1.1s (3 protons, C\(_{10}\)-CH\(_3\)), 0.68s (3 protons, C\(_{13}\)-CH\(_3\)), 0.33, 0.92 (other methyl protons); \( M^+ \) 370 (C\(_{27}\)H\(_{46}\)).

3\( \beta \)-Hydroxy-5\( \alpha \),6\( \beta \)-dibromocholestan-3-one

To a solution of cholesterol (5 g) in ether (30 ml) was added a bromine solution (0.9 ml of bromine in 20 ml of acetic acid containing 0.2 g of fused sodium acetate). The solution turned yellow and promptly set to a stiff paste. The mixture was cooled to 20° and stirred with a glass rod for about 5 minutes to ensure complete crystallization. The product was collected by filtration under suction and washed with cooled acetic acid. The air-dried product (6.9 g) melted at 112-113° (Lit. 189 m.p. 113°).

5\( \alpha \),6\( \beta \)-Dibromocholestan-3-one

The uncrystallized cholesteryl dibromide (6.3 g) was suspended in acetone (150 ml) in a three-necked round bottomed
flask fitted with a stirrer and a dropping funnel. The suspension was cooled in an ice bath and Jones' reagent\textsuperscript{184} (10 ml) was added dropwise, with stirring, over a period of 30 minutes. The temperature of the reaction mixture was maintained between 0-5\textdegree C by external cooling. After the addition was complete, stirring was continued for 15 minutes and cold water (200 ml) was added. The solid product was collected by filtration under suction, washed thoroughly with water, and methanol (ca 40 ml) and air-dried (5 g), m.p. 73-75\textdegree C (decomp.) (Lit.\textsuperscript{189} m.p. 73-75\textdegree C).

Cholest-5-en-3-one

To a solution of 5\alpha,6\beta-dibromocholestan-3-one (5 g) in ether (100 ml) and acetic acid (30 ml), zinc dust (7 g) was added in small portions during 20 minutes with continuous shaking. After the addition was complete the mixture was shaken for additional 10 minutes and zinc dust was filtered under suction. The filtrate was washed with water, sodium bicarbonate solution (5\%) and water and dried over anhydrous sodium sulphate. Evaporation of the solvent gave cholest-5-en-3-one as an oil, which crystallized from methanol (3 g), m.p. 128-129\textdegree C (Lit.\textsuperscript{189} m.p. 129\textdegree C).
Cholest-4-en-3-one (LX)

A solution of cholest-5-en-3-one (5 g) in ethanol (50 ml) containing oxalic acid (6 g) was heated under reflux for 15 minutes. The reaction mixture was poured into water and extracted with ether. The ether extract was washed with water, sodium bicarbonate solution (5%) and water and dried over sodium sulphate (anhydrous). The oily residue obtained after evaporation of the solvent was crystallized from ethanol to give cholest-4-en-3-one (LX) (3.8 g), m.p. 80-82° (Lit. 189 m.p. 81-82°).

Lithium aluminium hydride-aluminium chloride reduction of cholest-4-en-3-one (LX)

To a well stirred mixture of LiAlH₄ (2 g) and anhydrous AlCl₃ (7 g) in sodium dried ether (100 ml) was added an ethereal solution of the ketone (LX) (2 g) dropwise over a period of 30 minutes. After the addition was complete, the reaction mixture was kept at reflux temperature for 4 hours. A mixture of ethyl acetate and moist ether (cold) was then added to destroy the excess of the reducing agent and the aluminium complexes were decomposed by careful addition of cold, dilute sulphuric acid. The ethereal layer was separated, washed with dilute sulphuric acid, water, sodium bicarbonate
solution (5%) and water and dried over anhydrous sodium sulphate. Removal of the solvent gave an oil (ca 2 g) which was chromatographed over alumina (60 g; NCL grade). Each fraction of 25 ml was collected. Elution with light petroleum-ether (20:1) gave cholest-4-ene, crystallized from methanol (1.4 g), m.p. and m.m.p. 80-82°.

Chromic acid oxidation of cholest-4-ene; 5-keto-4,5-secocholestan-4-oic acid (CXX), cholest-4-en-3-one (LX) and cholest-4-en-6-one (CXLl)

To a well stirred mixture of cholest-4-ene (10.8 g) and glacial acetic acid (120 ml), chromium trioxide solution (10 g of CrO₃ in 20 ml of 50% acetic acid) was added dropwise over a period of 2 hours with continuous stirring. The reaction mixture was maintained at a temperature of about 55° throughout. Upon completion of the addition of chromic acid solution, the mixture was stirred for an additional 2 hours. The excess of chromic acid was destroyed by methanol (10 ml) and most of the solvent was removed by distillation under reduced pressure at a bath temperature of about 40°. The residue, a dark green viscous mass was diluted with water and extracted with ether. The ethereal solution was extracted with sodium hydroxide solution (10%, 4 x 50 ml). The ethereal layer was washed with water and dried over anhydrous sodium sulphate.
The ether was evaporated and the oily residue (ca 5 g) was chromatographed over silica gel (100 g; NCL grade). Each fraction of 30 ml was collected. Elution with light petroleum-ether (9:1) gave an oil, which crystallized from methanol to give cholest-4-en-6-one (CXLII) (500 mg)\textsuperscript{185}, m.p. and m.m.p. 108\textdegree. Elution with light petroleum-ether (6:1) gave a colourless solid; recrystallization from ethanol afforded cholest-4-en-3-one (LX) (1.5 g)\textsuperscript{189}, m.p. and m.m.p. 81-82\textdegree.

The combined alkaline extract was acidified with hydrochloric acid and the liberated organic acid was extracted with ether. The ethereal solution was washed with water and dried over anhydrous sodium sulphate. Removal of the desiccant and the solvent provided a gum (ca 4.5 g) which was purified by chromatography over silica gel (90 g; NCL grade). Elution with light petroleum-ether (4:1 to 2:1) gave the seco acid (CXX) as an oil (3.5 g), which was found to be homogeneous by t.l.c. in different solvent systems; \( \lambda_{\text{max}} \) 3400-3200br (COOH), 1710s, 1705s cm\(^{-1}\) (C=O and COOH); \( \delta \) (60 MHz) 10.0s (1 proton, disappeared on addition of D\(_2\)O, COOH), 2.3m (4 protons, COCH\(_2\) and CH\(_2\)COOH), 1.08s (3 protons, C\(_{10}\)-CH\(_3\)), 0.68s (3 protons, C\(_{13}\)-CH\(_3\)), 0.82, 0.90 (other methyl protons); \( M^+ \) 418 (C\(_{27}\)H\(_{46}\)O\(_3\)).
Methyl 5-keto-4,5-secocholestan-4-oate (CCLXXXVII)

An ethereal solution of the seco acid (CXX)(2 g) was treated with an excess of an ethereal solution of diazomethane in the cold. After usual work up of the reaction mixture the desired methyl ester (CCLXXXVII) was obtained as an oil (ca 2 g) which was purified by chromatography over silica gel (40 g; NCL grade). Elution with light petroleum-ether (10:1) gave the pure ester (1.5 g; homogeneous by t.l.c.); $\gamma_{\text{max}}$ 1735 s (COOCH$_3$), 1708 s cm$^{-1}$ (C=O); $\delta$ (60 MHz) 3.56 s (3 protons, COOCH$_3$), 2.2 m (4 protons, COCH$_2$ and CH$_2$COOCH$_3$), 1.0 s (3 protons, C$_{10}$-CH$_3$), 0.68 s (3 protons, C$_{13}$-CH$_3$), 0.83, 0.90 (other methyl protons).

Attempted preparation of 4a-oxa-A-homocholest-5-en-4-one (CXXCI)

(i) Reaction of the seco acid (CXX) with acetic anhydride-sodium acetate

The seco acid (CXX)(1 g) in acetic anhydride (30 ml, freshly distilled) was heated under reflux for 2 hours. The reaction mixture was allowed to attain room temperature and freshly fused sodium acetate (ca 0.2 g) was added and the heating continued for 6 hours. The acetic anhydride was removed by distillation under reduced pressure and the residue taken up in ether. The ethereal solution was washed with
water, sodium bicarbonate solution (5%) and water and dried over anhydrous sodium sulphate. Removal of the solvent gave a pale yellow oil (ca 1 g) which was subjected to chromatography over silica gel (29 g; NCL grade). Each fraction of 20 ml was collected. Eluates from light petroleum gave A-norcholesterol-3-ene (CCXCVII), which crystallized from methanol (170 mg), m.p. 78–80° (Lit.178 m.p. 80°); positive tetranitromethane test; $\nu_{\text{max}}$ 3050 cm$^{-1}$ (C=H), 1630 cm$^{-1}$ (C=C); $\delta$ (60 MHz) 5.3t (1 proton, C$_3$-H, vinylic proton), 1.0s (3 protons, C$_{10}$-CH$_3$), 0.70s (3 protons, C$_{13}$-CH$_3$), 0.92, 0.82 (other methyl protons).

Elution with light petroleum–ether (4:1) gave the unreacted seco acid (CXX) (ca 700 mg); no other product was obtained.

(ii) Reaction of the seco acid (CXX) with acetic anhydride–acetyl chloride:5-Acetoxy-4,5-secocholest-5-en-4-oic acid (CCXCVIII)

The seco acid (CXX)(1 g) in acetic anhydride (6 ml) and acetyl chloride (0.2 ml) was heated under reflux for 4 hours under anhydrous conditions. The acetic anhydride was removed by distillation under reduced pressure and the residue taken up in ether. The ethereal extract was washed with water, sodium bicarbonate solution (5%) and water and dried over
anhydrous sodium sulphate. Removal of the desiccant and the solvent provided an oil (ca 1 g) which was found to be a mixture of at least 2 components by t.l.c. It was subjected to chromatography over silica gel (20 g; NCL grade). Each fraction of 20 ml was collected. Elution with light petroleum gave 4-norcholest-3-ene (CCXCVII)(170 mg), m.p. and m.m.p. 78-80º.

Elution with light petroleum-ether (10:1) gave 5-acetoxy-4,5-secocholest-5-en-4-oic acid (CCXCVIII), crystallized from methanol (300 mg), m.p. 95º. (A mixed m.p. determination with the enol lactone CXIII showed depression). (Found: C, 75.44; H, 10.24. C_{29}H_{48}O_{4} requires C, 75.65; H, 10.48%)

\[ \text{\( \delta_{\text{max}} \)} \text{ 3400-3200 br (COOH), 3030 w (C=C-H), 1770 s (C=C-O-CO-CH}_3, \text{ enol acetate carbonyl), 1705 s (COOH), 1660 m cm}^{-1} (C=C=O); \]

\[ \delta (60 \text{ MHz}) 8.6 s (1 \text{ proton, disappeared on addition of D}_2O, \text{ COOH), 5.4 m (1 \text{ proton, } C_6-H, \text{ vinylic proton), 2.3 br (2 \text{ protons, CH}_2\text{COOH), 2.1 s (3 \text{ protons, CH}_3\text{COO), 0.98 s (3 protons, } C_{10}\text{-CH}_3), 0.68 s (3 \text{ protons, } C_{13}\text{-CH}_3), 0.92, 0.82 (other methyl protons); } \]

M* 460 \text{ (C}_{29}H_{48}O_{4}).

Methyl 5-acetoxy-4,5-secocholest-5-en-4-oate (CCXCIX)

The seco acid (CCXCVIII)(100 mg) in ice cooled ether (20 ml) was treated with an ethereal solution of diazomethane. After usual work up of the reaction mixture the desired methyl
ester (CCXCIX) was obtained as an oil which crystallized from light petroleum (60 mg), m.p. 115°. (Found: C, 75.80; H, 10.30. C_{30}H_{50}O_{4} requires C, 75.98; H, 10.54%). \( \delta_{\text{max}} \) 1770s (\( \text{C} = \text{O} \rightarrow \text{C} \rightarrow \text{O} \), enol acetate carbonyl), 1740s (\( \text{COOCH}_3 \)), 1660m cm^{-1} (\( \text{C} = \text{O} \)); \( \delta \) (60 MHz) 5.5m (1 proton, \( \text{C}_6-\text{H} \), vinylic proton), 3.6s (3 protons, \( \text{COOCH}_3 \), 2.54br (2 protons, \( \text{CH}_2\text{COOCH}_3 \)), 2.08s (3 protons, \( \text{CH}_3\text{COO} \), 1.0s (3 protons, \( \text{C}_{10}-\text{CH}_3 \)), 0.70s (3 protons, \( \text{C}_{13}-\text{CH}_3 \)), 0.94, 0.82 (other methyl protons); \( M^+ \) 474 (\( \text{C}_{30}\text{H}_{50}O_{4} \)).

Hydrolysis of methyl 5-acetoxy-4,5-secocholest-5-en-4-oate (CCXCIX); 5'-keto-4,5-secocholestan-4-oic acid (CXX)

The methyl ester (CCXCIX) (100 mg) was heated under reflux with methanolic KOH (20 ml, 5%) for 1 hour. Most of the solvent was removed by distillation under reduced pressure and the residue diluted with water and acidified with hydrochloric acid. The organic product was extracted with ether and the ethereal solution washed with water and dried over anhydrous sodium sulphate. Removal of the solvent gave the seco acid (CXX) which was purified by chromatography (silica gel). The seco acid (CXX) (65 mg) thus obtained was found to be identical with an authentic sample.
Hydrolysis of 5-acetoxy-4,5-secocholest-5-en-4-0ic acid (CCXCVIII)

The enol acetate (CCXCVIII) (80 mg) was hydrolysed in the manner described above to provide the seco acid (CXX) (ca 55 mg).

Baeyer-Villiger oxidation of methyl 5-keto-5,6-secocholestan-6-oate (CX): Methyl 5a-oxa-5-keto-5,6-seco-A-homocholestan-6-oate (CCCII) and 5a-oxa-5-keto-5,6-seco-A-homocholestan-6-oic acid (CCCIII)

To a solution of the methyl ester (CX) (2 g) in chloroform (10 ml), a chloroform solution of perbenzoic acid (2.5 mole equiv.) and a few crystals of p-toluenesulphonic acid monohydrate were added. The reaction mixture was kept in the dark for 96 hours at room temperature. The progress of the reaction was checked by t.l.c. The reaction mixture was diluted with water and the organic layer separated. The chloroform solution was washed with sodium bicarbonate solution (5%) and water and dried over anhydrous sodium sulphate. Removal of the solvent under reduced pressure gave an oil (ca 2 g) which was chromatographed over silica gel (40 g; NCL grade). Each fraction of 20 ml was collected. Elution with light petroleum did not give any product. Elution with light petroleum-ether (10:1) gave the unreacted ester (CX) (ca 200 mg), m.p. and m.m.p. 102°. Elution with light petroleum-ether (5:1) gave methyl 5a-oxa-
5-keto-5,6-seco-A-homocholestan-6-oate (CCCI) as an oil
(600 mg) (homogeneous by t.l.c.). (Found: C, 74.80; H, 10.52.
C_{25}H_{48}O_{4} requires C, 75.00; H, 10.71%). \( \gamma_{\text{max}} \) 1740 s (\text{COOCH}_3),
1720 s cm\(^{-1}\) (\(\epsilon\)-lactone carbonyl); \(\delta\) (60 MHz) 3.57 s (3 protons,
\text{COOCH}_3), 2.3 br (4 protons, \text{CH}_2\text{COOCH}_3 and \text{CH}_2\text{COO}), 1.28 s
(3 protons, \text{C}_{10}\text{CH}_3), 0.67 s (3 protons, \text{C}_{13}\text{CH}_3), 0.88, 0.86,
0.80 (other methyl protons); M\(^+\) 448 (C_{28}H_{48}O_{4}).

Elution with light petroleum-ether (3:1) gave the seco
acid (CVII) (ca 150 mg). Further elution with light petroleum-
ether (1:2 to 1:4) yielded 5a-oxa-5-keto-5,6-seco-A-homo-
cholestan-6-oic acid (CCCIII) as a homogeneous oil (300 mg).
(Found: C, 74.55; H, 10.58. C_{27}H_{46}O_{4} requires C, 74.65;
H, 10.6%); \( \gamma_{\text{max}} \) 3450-3200 br (\text{COOH}), 1720 s (\(\epsilon\)-lactone
carbonyl), 1705 s cm\(^{-1}\) (\text{COOH}); \(\delta\) (60 MHz) 9.2 s (1 proton,
disappeared on addition of D\(_2\)O, \text{COOH}), 2.2 br (4 protons,
\text{CH}_2\text{COOH and CH}_2\text{COO}), 1.29 s (3 protons, \text{C}_{10}\text{CH}_3), 0.68 s
(3 protons, \text{C}_{13}\text{CH}_3), 0.88, 0.85, 0.80 (other methyl protons);
M\(^+\) 434 (C_{27}H_{46}O_{4}).

Methylation of 5a-oxa-5-keto-5,6-seco-A-homocholestan-
6-oic acid (CCCIII)

The lactone acid (CCCIII) (120 mg) was treated with an
excess of an ethereal solution of diazomethane in the cold and
the reaction mixture worked up in the usual manner to provide
the lactone ester (CCCII) (90 mg). This was found to be identical with the lactone ester (CCCII) obtained in the previous experiment.

**Ferbenzoic acid oxidation of methyl 5-keto-4,5-secocholestan-4-oate (CCLXXXVII):** Methyl 5-oxa-6-keto-4,5-seco-B-homocholestan-4-oate (CCCVI), 5-oxa-6-keto-4,5-seco-B-homocholestan-4-oic acid (CCCVII) and methyl 6-oxa-5-keto-4,5-seco-B-homocholestan-4-oate (CCCVIII)

To a solution of the methyl ester (CCLXXXVII) (3 g) in chloroform (15 ml), a chloroform solution of perbenzoic acid (2.5 mole equiv.) and a few crystals of p-toluenesulphonic acid were added and the reaction mixture kept at room temperature for 96 hours. Most of the solvent was removed by distillation under reduced pressure and the residue dissolved in ether. The ethereal solution was washed with water, sodium bicarbonate solution (5%) and water and dried over anhydrous sodium sulphate. Removal of the solvent provided an oil (ca 2.9 g) which was chromatographed over silica gel (60 g; NCL grade). Each fraction of 20 ml was collected. Elution with light petroleum did not give any organic product. Elution with light petroleum-ether (10:1) gave the unreacted methyl ester (CCLXXXVII) (200 mg). Elution with light petroleum-ether (4:1 and 3:1) gave methyl 5-oxa-6-keto-4,5-seco-B-homocholestan-4-oate (CCCVI) as a homogeneous oil (700 mg).
(Found: C, 74.7; H, 10.5. \( \text{C}_{28}\text{H}_{48}\text{O}_{4} \) requires C, 75.0; 
H, 10.71%); \( \gamma_{\text{max}} \) 1740s (COOCH\(_3\)), 1720s cm\(^{-1}\) (\( \epsilon \)-lactone 
carbonyl); \( \delta \) (60 MHz) 3.6s (3 protons, COOCH\(_3\)), 2.4br 
(4 protons, CH\(_2\)COOCH\(_3\) and CH\(_2\)COO), 1.28s (3 protons, \( \text{C}_{10}-\text{CH}_3 \)), 
0.70s (3 protons, \( \text{C}_{13}-\text{CH}_3 \)), 0.96, 0.94 (other methyl protons); 
M\(^+\) 448 (\( \text{C}_{28}\text{H}_{48}\text{O}_{4} \)).

Elution with light petroleum-ether (2:1) gave methyl 
6-oxa-5-keto-4,5-seco-\( \beta \)-cholestan-4-oate (CCCXI) (120 mg) 
as a noncrystallizable oil. (Found: C, 74.82; H, 10.52.
\( \text{C}_{28}\text{H}_{48}\text{O}_{4} \) requires C, 75.0; H, 10.71%); \( \gamma_{\text{max}} \) 1742s (COOCH\(_3\)), 
1720s cm\(^{-1}\) (\( \epsilon \)-lactone carbonyl); \( \delta \) (60 MHz) 3.84m (2 protons, 
CH\(_2\)-O-CO), 3.5s (3 protons, COOCH\(_3\)), 2.26m (2 protons, CH\(_2\)COOCH\(_3\)), 
1.06s (3 protons, \( \text{C}_{10}-\text{CH}_3 \)), 0.68s (3 protons, \( \text{C}_{13}-\text{CH}_3 \)), 0.94, 
0.82 (other methyl protons); M\(^+\) 448 (\( \text{C}_{28}\text{H}_{48}\text{O}_{4} \)).

Elution with light petroleum-ether (1:1) gave the seco 
acid (CXX) (200 mg). Continued elution with light petroleum- 
ether (1:2 to 1:4) gave 5-oxa-6-keto-4,5-seco-\( \beta \)-cholestan-
4-oic acid (CCCXII) (130 mg) as a noncrystallizable oil.
(Found: C, 74.55; H, 10.58. \( \text{C}_{27}\text{H}_{46}\text{O}_{4} \) requires C, 74.65; 
H, 10.60%); \( \gamma_{\text{max}} \) 3430-3250br (COOH), 1722s (\( \epsilon \)-lactone 
carbonyl), 1708s cm\(^{-1}\) (COOH); \( \delta \) (60 MHz) 10.1s (1 proton, 
disappeared on addition of D\(_2\)O, COOH), 2.3br (4 protons, 
CH\(_2\)COOH and CH\(_2\)COO), 1.29s (3 protons, \( \text{C}_{10}-\text{CH}_3 \)), 0.70s 
(3 protons, \( \text{C}_{13}-\text{CH}_3 \)), 0.94, 0.82 (other methyl protons); 
M\(^+\) 434 (\( \text{C}_{27}\text{H}_{46}\text{O}_{4} \)).
Methylation of 5-oxa-6-keto-4,5-seco-8-homocholestan-4-oic acid (CCCVII)

The lactone acid (CCCVII)(100 mg) in ether (20 ml) was treated with an excess of an ethereal solution of diazomethane in the cold. After usual work up of the reaction mixture, the methyl ester (CCCVI)(80 mg) was obtained which was found to be identical with the previously obtained sample of (CCCVI).

Reaction of methyl 5-keto-5,6-secocholestan-3-en-6-oate (CCLXXXIX) with perbenzoic acid; Methyl 3\(\alpha,4\alpha\)-epoxy-5-keto-5,6-secocholestan-6-oate (CCCIIX) and methyl 5,6-seco-3\(\alpha,4\alpha\)-epoxy-5-keto-5a-oxa-A-homocholestan-6-oate (CCCX).

To a solution of the seco acid (CCLXXXIX)(3.5 g) in chloroform (25 ml), a chloroform solution of perbenzoic acid (2.5 mole equiv.) and a few crystals of p-toluenesulphonic acid were added and the reaction mixture allowed to stand at room temperature for 4 days. After usual work up of the reaction mixture, an oil (ca 3.4 g) was obtained which was chromatographed over silica gel (70 g; NCL grade). Each fraction of 20 ml was collected. Eluates from light petroleum-ether (10:1) gave the unreacted methyl ester (CCLXXXIX) (180 mg). Elution with light petroleum-ether (4:1) gave the epoxide, methyl 3\(\alpha,4\alpha\)-epoxy-5-keto-5,6-secocholestan-6-oate (CCCIIX)(700 mg) as an oil. (Found: C, 75.10; H, 10.20.
C_{28}H_{46}O_{4} requires C, 75.33; H, 10.31%; \nu_{\text{max}} \text{ 1740s (COOCH}_3\text{), 1710s (C=O), 870m cm}^{-1} \text{ (epoxide); U.v. featureless in the region 220-360 nm; } \delta \text{ (60 MHz) 3.6s (3 protons, COOCH}_3\text{), 3.36d like (1 proton, J=5 Hz, C}_4\text{-H), 3.2m (1 proton, C}_3\text{-H), 2.3br (2 protons, CH}_2\text{COOCH}_3\text{), 1.1s (3 protons, C}_1\text{CH}_3\text{), 0.75s (3 protons, C}_1\text{CH}_3\text{), 0.96, 0.84 (other methyl protons).}

Elution with light petroleum-ether (3:1 to 2:1) gave the epoxy lactone, methyl 5,6-seco-3\alpha,4\alpha\epsilon\text{-epoxy-5-keto-5a-oxa-A-homocholestan-6-oate (CCCX)} \text{(200 mg) as a noncrystallizable oil (Found: C, 72.65; H, 9.5. C}_{28}H_{46}O_{5} \text{ requires C, 72.72; H, 9.9%); U.v. featureless in the region 220-360 nm; } \nu_{\text{max}} \text{ 1740s (COOCH}_3\text{), 1718s (\epsilon-lactone carbonyl), 870m cm}^{-1} \text{ (epoxide); } \delta \text{ (60 MHz) 3.58s (3 protons, COOCH}_3\text{), 3.3m (2 protons, C}_3\text{-H and C}_4\text{-H), 2.3br (2 protons, CH}_2\text{COOCH}_3\text{), 1.3s (3 protons, C}_1\text{CH}_3\text{), 0.70s (3 protons, C}_1\text{CH}_3\text{), 0.92, 0.81 (other methyl protons); M^+ 462 (C}_{28}H_{46}O_{5}). \text{ Elution with light petroleum-ether (1:1 to 1:2) gave the seco acid(CCLXXXVIII) (ca 200 mg).}

Reaction of the seco acid, 5-keto-5,6-secocholest-3-en-6-oic acid (CCLXXXVIII) with benzoyl chloride-pyridine; Attempted preparation of the \beta-lactone, 5\beta-hydroxy-B-norcholest-3-en-6-oic acid, 5,6-lactone (CCCXIII)

The seco acid (CCLXXXVIII)(1.6 g) was dissolved in pyridine (8 ml) and to the resultant solution, benzoyl chloride
(2 ml) was added. The reaction mixture was allowed to stand at room temperature for 96 hours. It was poured into crushed ice-water mixture and extracted with ether. The ethereal solution was washed successively with water, dilute hydrochloric acid, water, sodium bicarbonate solution (5%), and water and dried over anhydrous sodium sulphate. Removal of the solvent gave an oil (1.4 g) which was chromatographed over silica gel (30 g; NCL grade). Each fraction of 20 ml was collected. Elution with light petroleum gave B-norcholesta-3,5-diene (CXCIII) (700 mg), m.p. and m.m.p. 76°. (I.r. spectra of the various subsequent fractions were determined but none of them showed a peak at about 1820 cm⁻¹ thus showing the absence of the 3-lactone (CCCXIII). However, the i.r. spectrum of the crude product showed a weak peak at 1765 cm⁻¹ which indicated the presence of the dienol lactone (CCXC) in trace amounts).

Elution with light petroleum-ether (4:1 to 3:1) gave the unreacted acid (CCLXXXVII) (ca 500 mg).

Reaction of the seco acid, 5-keto-4,5-secocholestan-4-oic acid (CXX) with benzoyl chloride-pyridine: Attempted preparation of the β-lactone, 5β-hydroxy-A-norcholestan-4-oic acid 4,5-lactone (CCCXIV)

The seco acid (CXX) (1 g) in pyridine (5 ml) was treated with benzoyl chloride (1.5 ml) and the reaction mixture allowed
to stand at room temperature for 72 hours. It was worked up in the manner described in the preceding experiment, to give an oil (0.9 g) which was chromatographed over silica gel (20 g; NCL grade). Each fraction of 20 ml was collected.

Eluates from light petroleum gave A-norcholest-3-ene (CCXCVII) (400 mg), m.p. and m.m.p. 79°. Elution with light petroleum-ether (4:1) gave the unreacted acid (CXX)(300 mg). Elution with light petroleum-ether (3:1 to 1:2) gave traces of oily products. Although the i.r. spectra of the various fractions were determined but none of them showed the presence of the desired β-lactone (CCCV). However, the i.r. spectra of one or two fractions gave indication of the presence of the enol benzoate (CCCVII) but only in trace amounts.

**Attempted conversion of 6-oxa-B-homocholest-4-en-7-one (CXXXII) to B-norcholest-5-ene (CIX)**

(i) **With acetic anhydride-sodium acetate.**

The enol lactone (CXXXII)(50 mg) was heated under reflux with acetic anhydride (5 ml) and fused sodium acetate (ca 10 mg) for 4 hours. After usual work up of the reaction mixture, a solid was obtained which was recrystallized from light petroleum to give the unchanged enol lactone (CXXXII) (40 mg), m.p. and m.m.p. 94°.
(ii) **With heat.**

The enol lactone (CXIII) was heated in an oil bath at 140-150° for 30 minutes. There was no indication of evolution of any gaseous product. The melt was allowed to attain room temperature. From the t.l.c. of the solidified melt it was evident that the lactone (CXIII) has remained unchanged. Recrystallization from light petroleum gave (CXIII) (42 mg), m.p. and m.m.p. 94°.

(iii) **With benzoyl chloride-pyridine.**

The enol lactone (CXIII)(100 mg) was dissolved in pyridine (4 ml) and benzoyl chloride (0.5 ml) was added to the solution. The reaction mixture was allowed to stand at room temperature for 70 hours. The reaction mixture was worked up in the usual manner to give an oil (ca 80 mg) which was chromatographed over silica gel (3 g; NCL grade). Eluates from light petroleum gave B-norcholest-5-ene (CIX)(50 mg), m.p. and m.m.p. 68°.

**Attempted decarboxylation of the enol lactone, 3β-acetoxy-6-oxa-B-homocholest-4-en-7-one (XCIX)**

(i) **With heat.**

The enol lactone (XCIX)(50 mg) was heated in an oil bath at 140-150° for 30 minutes. There was no evidence for
evolution of CO₂. The melt was allowed to attain room temperature. From t.l.c. and spectral data it was found to be the unchanged enol lactone (XCIX) (45 mg).

(ii) **With benzoyl chloride-pyridine.**

The enol lactone (XCIX) (100 mg) was dissolved in pyridine (4 ml) and benzoyl chloride (0.5 ml) was added to the solution and the reaction mixture allowed to stand at room temperature for 70 hours. After usual work up of the reaction mixture, the residue was crystallized from light petroleum to give 3β-acetoxy-β-norcholest-5-ene (C) (55 mg), m.p. and m.m.p. 80-81°.

(iii) **With acetic anhydride-sodium acetate.**

The enol lactone (XCIX) (50 mg) was heated under reflux with acetic anhydride (5 ml) and fused sodium acetate (ca 10 mg) for 4 hours. After the usual work up of the reaction mixture the unchanged enol lactone (XCIX) was obtained (ca 40 mg). The recovered material was identical in all respects with the starting enol lactone (XCIX).
PART - II

Reaction of methyl 5-keto-4,5-secocholestan-4-oate (CCLXXXVII) with hydrazoic acid

(i) In polyphosphoric acid.

A mixture of the methyl ester (CCLXXXVII) (1 g) in polyphosphoric acid (60 g, freshly prepared) was heated to a temperature of 55-60°C on a water bath and sodium azide (150 mg) added in small portions with stirring. The reaction mixture was kept at this temperature for 10 hours and then poured onto crushed ice with stirring. It was extracted with chloroform (150 ml x 3) and the organic extract washed with water, sodium bicarbonate solution (5%) and water and dried over anhydrous sodium sulphate. Removal of the desiccant and the solvent gave an oil (ca 1 g), which was chromatographed over silica gel (20 g; NCL grade). Each fraction of 20 ml was collected. Elution with light petroleum did not give any product. Eluates from light petroleum-ether (10:1) gave the unreacted methyl ester (CCLXXXVII) (ca 100 mg). Elution with light petroleum-ether (4:1 to 3:1) gave the seco acid (CXX) (80 mg), the hydrolysed product of the methyl ester (CCLXXXVII). Elution with chloroform yielded methyl 5-aza-6-keto-4,5-seco-B-homocholestan-4-oate (CCXCVI) (300 mg), recrystallized
from methanol, m.p. 155°. (Found: C, 74.98; H, 10.8. C_{28}H_{49}O_{4}N requires C, 75.39; H, 10.96%); \( \gamma_{\text{max}} \) 3310w, 3230m, 3080m (NH), 1745s (COOCH_{3}), 1652s cm^{-1} (N-C=O); \( \delta \) (60 MHz) 5.92br,s (1 proton, disappeared on addition of D_{2}O, CONH), 3.68s (3 protons, COOCH_{3}), 2.3br,m (4 protons, CH_{2}COOCH_{3} and CH_{2}CO-N-), 1.35s (3 protons, C_{10}-CH_{3}), 0.70s (3 protons, C_{13}-CH_{3}), 0.32, 0.96 (other methyl protons).

Elution with chloroform-methanol (10:1) gave 5-aza-6-keto-4,5-seco-3-homocholestan-4-oic acid (CCCXVIII), crystallized from ether (170 mg), m.p. 135°. (Found: C, 74.75; H, 10.75. C_{27}H_{47}O_{3}N requires C, 74.82; H, 10.35%); \( \gamma_{\text{max}} \) 3250-3400br (COOH) with merging peaks at 3230m, 3100m (NH), 1705s (COOH), 1655s cm^{-1} (CO-N); \( \delta \) (60 MHz) 6.3br (2 protons, COOH and CONH, rapidly exchanging protons between themselves disappeared on addition of D_{2}O), 2.35br (4 protons, CH_{2}COOH and CH_{2}CON-), 1.34s (3 protons, C_{10}-CH_{3}), 0.88s (3 protons, C_{13}-CH_{3}), 0.32, 0.94 (other methyl protons).

(ii) In conc. sulphuric acid.

To a solution of the methyl ester (CCLXXXVII)(1 g) and sulphuric acid (1.2 ml) in sodium dried benzene (7 ml), sodium azide (150 mg) was added slowly with stirring at room temperature. A brisk reaction ensued and after 1 hour the reaction mixture was poured onto crushed ice with stirring.
The benzene layer was separated and the aqueous layer extracted with chloroform. After usual work up of the organic extract, an oil (ca 1 g) was obtained which was subjected to column chromatography over silica gel (20 g; NCL grade). Each fraction of 20 ml was collected. Elution with light petroleum-ether (10:1) gave the unreacted methyl ester (CCLXXXVII) (120 mg). Eluates from light petroleum-ether (4:1) gave the seco acid (CXX)(75 mg). Elution with chloroform afforded the lactam (CCXCVI), crystallized from chloroform (330 mg), m.p. and m.m.p. 155°. Elution with chloroform-methanol (10:1) gave the lactam acid (CCCXVIII), crystallized from ether (150 mg), m.p. and m.m.p. 135°.

**Methylation of 5-aza-6-keto-4,5-seco-B-homocholestan-4-oic acid (CCCXVIII)**

The lactam acid (CCCXVIII)(80 mg) in ether (40 ml) was treated with an excess of an ethereal solution of diazomethane in the cold. After the usual work up of the reaction mixture, a solid was obtained which crystallized from chloroform to afford the lactam ester (CCXCVI)(60 mg), m.p. and m.m.p. 155°.
Oximation of 5-keto-4,5-secocholestan-4-oic acid (CXX)

A mixture of the seco acid (CXX) (1.5 g), hydroxylamine hydrochloride (1.5 g), potassium hydroxide (1.5 g), water (5 ml) and ethanol (100 ml) was heated under reflux for 4 hours. Most of the solvent was removed by distillation under reduced pressure and the residue diluted with water, acidified (HCl) and extracted with ether. The ethereal layer was washed with water, sodium bicarbonate solution (5%), and water and dried over sodium sulphate (anhydrous). Removal of the desiccant and the solvent gave an oil (1.2 g) which crystallized from light petroleum to give the corresponding oxime (CCCXX) (800 mg), m.p. 163° (Lit. 179 165-166°); \( \delta_{\text{max}} \)
3300s, br (COOH and N-OH), 1700s (COOH), 1650w cm\(^{-1}\) (C=N-OH);
\( \delta(60 \text{ MHz}) \) 9.8br (2 protons, disappeared on shaking with D\(_2\)O, COOH and N-OH), 1.06s (3 protons, C\(_{10}\)-CH\(_3\)), 0.68s (3 protons, C\(_{13}\)-CH\(_3\)), 0.90, 0.80 (other methyl protons).

Beckmann rearrangement of the oxime (CCCXX)

The oxime (CCCXX) (700 mg) was added as quickly as possible, with stirring, to thionyl chloride (8 ml) at 0° and the solution was immediately poured into 4N potassium hydroxide solution (60 ml) kept at 80°. A solid thus obtained was filtered under suction, washed with water and air-dried. The crude product (ca 700 mg) thus obtained was subjected to column
chromatography over silica gel (12 g; NCL grade). Each fraction of 20 ml was collected. Elution with light petroleum-ether (4:1) gave the seco acid (CXX) in traces (by t.l.c.). Elution with light petroleum-ether (3:1) gave the unreacted oxime (CCCXX)(100 mg), m.p. and m.m.p. 163°. Elution with chloroform-methanol (10:1) gave the lactam acid, 5-aza-6-keto-4,5-seco-B-homocholestan-4-oic acid (CCCXVIII), crystallized from ether (200 mg), m.p. and m.m.p. 135°.

**Oximation of methyl 5-keto-4,5-secocholestan-4-oate (CCLXXXVII)**

A mixture of the methyl ester (CCLXXXVII)(1 g), hydroxylamine hydrochloride (1 g), sodium acetate trihydrate (2 g), water (4 ml) and ethanol (80 ml) was heated under reflux for 4 hours. Most of the solvent was removed by distillation under reduced pressure and the residue diluted with water and extracted with ether. The usual work up of the ethereal solution provided an oil (ca 900 mg) which crystallized from light petroleum to give the oxime (CCCXXI)(620 mg), m.p. 87°. (Found: C, 75.00; H, 10.82. C_{28}H_{49}O_{3}N requires C, 75.16; H, 10.96%); \( \epsilon_{max} \) 3400s (N-OH), 1743s (COO-CH₃), 1655w cm⁻¹ (C=N-OH); \( \delta \) (60 MHz) 7.2br,s (1 proton, disappeared on addition of D₂O, N-OH), 3.58s (3 protons, COOCH₃), 1.02s (3 protons, C_{10}-CH₃), 0.68s (3 protons, C_{13}-CH₃), 0.91, 0.82 (other methyl protons).

Methylation of the acid oxime (CCCXX), m.p. 163° with diazomethane also gave the oxime (CCCXXI), m.p. and m.m.p. 87°.
Beckmann rearrangement of the methyl ester oxime (CCCXXXI)

The methyl ester oxime (CCCXXXI)(800 mg) was added as quickly as possible to thionyl chloride (10 ml) with stirring at 0° and the resultant solution was poured into hot (80°) 4N potassium hydroxide solution (80 ml). A solid thus obtained was filtered under suction, washed with water and air-dried. The crude product (700 mg) was chromatographed over silica gel (14 g; NCL grade). Each fraction of 20 ml was collected. Elution with light petroleum did not give any product. Eluates from light petroleum-ether (7:1) gave the unreacted oxime (CCCXXXI)(95 mg), m.p. and m.m.p. 87°. Elution with chloroform gave the lactam (CCXCVI)(300 mg), m.p. and m.m.p. 155°. Eluates from chloroform-methanol (10:1) gave the lactam acid (CCXCVIII) (180 mg), m.p. and m.m.p. 135°.

Attempted Schmidt reaction of methyl 5-keto-5,6-secocholestan-6-oate (CX) with hydrazoic acid

(i) In polyphosphoric acid.

A mixture of the methyl ester (CX)(1 g) in polyphosphoric acid (60 g, freshly prepared) was heated to a temperature of 55–60° on a water bath and sodium azide (150 mg) was added in small portions with stirring. The reaction mixture was kept at this temperature for about 10 hours and then poured onto crushed ice with stirring. It was extracted with chloro-
form. After the usual work up of the chloroform solution, an oil (ca 1 g) was obtained which was chromatographed over silica gel (20 g; NCL grade). Each fraction of 20 ml was collected. Elution with light petroleum-ether (10:1) gave the unreacted methyl ester (CIX) (550 mg), m.p. and m.m.p. 102-103°. Elution with light petroleum-ether (5:1 to 4:1) gave the seco acid (CVII) (ca 250 mg). No other product was obtained in this reaction.

(ii) In conc. sulphuric acid.

To a solution of the methyl ester (CIX) (1 g) and sulphuric acid (1.2 ml) in sodium dried benzene (7 ml), sodium azide (150 mg) was added slowly at room temperature. A brisk reaction ensued and after 1 hour the reaction mixture was poured onto crushed ice. The benzene layer was separated and the aqueous layer extracted with chloroform. The combined organic extract was worked up in the usual manner to afford an oil (ca 1 g), which after chromatography over silica gel gave the unreacted methyl ester (CIX) (ca 600 mg), m.p. and m.m.p. 102° and the seco acid (CVII) (ca 250 mg); no other product was obtained.
Attempted oximation of 5-keto-5,6-secocholestan-6-oic acid (CVII)

A mixture of the seco acid (CVII) (1 g), hydroxylamine hydrochloride (1 g), potassium hydroxide (1 g), water (5 ml) and ethanol (80 ml) was heated under reflux for 4 hours. Most of the solvent was removed by distillation under reduced pressure and the residue worked up in usual manner. It gave an oil (ca 0.9 g) which was shown to be the unchanged acid (CVII) by t.l.c., spectral properties and conversion to the methyl ester (CX).

Attempted oximation of methyl 5-keto-5,6-secocholestan-6-oate (CX)

A mixture of the methyl ester (CX) (500 mg), hydroxylamine hydrochloride (500 mg), sodium acetate trihydrate (1 g), water (2 ml) and ethanol (40 ml) was heated under reflux for 4 hours. The reaction mixture was worked up in the manner described before. It provided the unreacted methyl ester (CX) (450 mg), recrystallized from methanol, m.p. and m.m.p. 102-103°.

Both the acid (CVII) and the ester (CX) thus failed to give the corresponding oximes.
PART - III

The mass spectra were measured on an AEI MS-9 mass spectrometer at 70 eV using a direct insertion technique at source temperature of about 200°C. The accurate mass measurement were relative to fragment ions of heptacosfluorotributyl amine at a resolving power of 15,000.

The values (m/e) of the fragment ions from various compounds are tabulated below. The values in parentheses are the relative abundance (%) of the peaks, with respect to base peak taken as 100% and the composition of fragment ions as determined by accurate mass measurement.

5-Keto-5,7-seco-6-norcholestan-7-oic acid (LXXXIV)

\[ M^+ 404 \text{ (1.05; C}_{26}\text{H}_{44}\text{O}_3} \], m/e 386(11.4), 376(0.5), 371(1.05), 360 (2.2), 358(1.05), 343(0.5), 319(0.8), 275(10.5), 273(0.9), 264(1.4), 247(5.00), 245(0.7), 233(0.7), 231(0.5), 163(1.86), 161(3.44), 135(7.9), 133(5.81), 121(5.58), 119(3.49), 112(100; C_{7\text{H}}_{12}O), 111(8.14), 110(8.14), 95(10.0), 93(8.84), 91(3.14), 83(9.07), 81(12.31), 79(7.00), 71(5.34), 69(4.42), 67(4.2), 57(11.4), 55(13.5),

Methyl-5-keto-5,7-seco-6-norcholestan-7-oate (LXXXIV-a)

\[ M^+ 418(0.941; C_{27}\text{H}_{46}\text{O}_3} \], m/e 400(0.353), 387(1.058), 386(1.30), 374(1.0), 371(0.401), 358(1.05), 343(0.401), 333(1.0), 331(0.47), 315(0.53), 314(0.47), 309(1.11), 307(2.23), 287(0.35), 275(2.35), 274 (1.29), 273(1.00), 247(2.17), 245(0.7), 231(0.6),
299(0.47), 217(0.82), 193(1.52), 166(2.00), 163(1.30),
161(2.11), 151(1.05), 149(1.11), 147(1.11), 135(3.41),
133(3.41), 121(2.58), 119(2.23), 112(100; C_7H_12O), 107(3.58),
105(2.33), 97(2.47), 95(4.53), 93(4.00), 91(2.00), 83(2.00),
81(4.5), 79(2.47), 71(2.01), 69(3.97), 67(2.82), 57(3.53),
55(6.35), 43(5.52), 41(4.47).

5-Keto-5,6-secocholestan-6-oic acid (CVII)

M⁺ 418 (very weak; C_{27}H_{46}O_3), m/e 400 (1.384), 390(0.307),
385(0.38), 374(1.7), 372(0.53), 359(1.7), 341(0.53), 333(1.23),
318(3.7), 314(0.80), 306(2.00), 305(3.00), 291(0.90), 289(0.53),
287(0.61), 277(0.53), 273(0.51), 265(0.38), 261(0.90), 247(4.46),
246(0.84), 245(0.91), 231(0.53), 217(0.84), 193(1.47), 167(1.23),
166(1.7), 153(3.07), 135(4.00), 133(4.61), 121(3.3), 119(2.80),
113(9.0), 112(100; C_7H_12O), 107(6.00), 105(4.1), 95(6.8),
93(4.61), 91(3.7), 83(7.53), 81(4.31), 79(4.31), 71(3.07),
69(8.77), 67(5.69), 57(11.3), 55(9.07), 43(11.6), 41(11.3).

Methyl 5-keto-5,6-secocholestan-6-oic acid (CX)

M⁺ 432(0.77; C_{28}H_{48}O_3), m/e 414(1.15), 401(1.02),
400(0.89), 398(1.29), 372(2.3), 359(2.3), 355(0.89), 330(1.02),
321(1.54), 320(2.56), 319(0.49), 305(1.02), 289(1.15), 279(1.15),
275(0.77), 247(9.48), 246(1.54), 245(1.30), 231(0.77), 217(1.8),
207(2.3), 180(2.43), 167(2.77), 163(1.53), 161(1.27), 149(2.3),
3β-Acetoxy-5,6-secocholestan-6-oic acid (XCVIII)

\[ \text{M}^+ 476 \text{(not present; C}_{29}\text{H}_{48}\text{O}_3), \text{m/e 416 M}^+\text{AcOH(1.26),}
\]
\[ \text{m/e 401(0.53), 398(0.62), 370(0.90), 357(1.07), 334(0.53),}
\]
\[ 331(1.25), 313(0.53), 306(0.98), 305(0.8), 291(0.53), 289(0.53),
\]
\[ 273(0.70), 247(2.14), 246(0.53), 193(1.07), 179(0.70), 175(0.70),
\]
\[ 166(1.07), 149(1.25), 147(1.25), 135(2.5), 133(3.21), 121(1.75),
\]
\[ 119(1.75), 110(100; C}_7\text{H}_{10}O), 109(5.79), 108(3.33), 107(3.5),
\]
\[ 105(2.28), 95(4.21), 93(4.03), 91(2.8), 83(1.75), 81(5.26),
\]
\[ 79(2.45), 71(3.33), 69(3.5), 68(11.9), 60(13.68), 57(4.56),
\]
\[ 55(5.78), 45(10.78), 43(11.9). \]

5-Keto-5,7-seco-6-norcholest-3-en-7-oic acid (LXXXII)

\[ \text{M}^+ 402(0.5; C}_{26}\text{H}_{42}\text{O}_3), \text{m/e 384(1.66), 356(0.5), 341(0.35),}
\]
\[ 317(1.66), 299(1.66), 289(0.83), 275(2.0), 273(0.66), 271(0.66),
\]
\[ 259(0.50), 247(1.0), 233(0.41), 231(0.41), 207(0.66), 205(0.66),
\]
\[ 179(0.66), 177(1.0), 175(1.0), 163(1.55), 161(1.16), 149(1.6),
\]
\[ 135(4.00), 133(3.0), 123(1.66), 121(2.66), 119(1.83), 110(100; \]
\[ C}_7\text{H}_{10}O), 109(6.0), 108(2.5), 107(4.0), 105(3.33), 95(6.66),
\]
Methyl 5-keto-5,6-secocholestan-3-en-7-oate (CCLXXXIX)

M⁺ 430(2.00; C₂₈H₄₆O₃), m/e 415(0.727), 412(1.63), 399(1.09), 398(1.09), 389(0.54), 370(1.09), 357(3.27), 353(0.54), 348(0.45), 330(0.45), 321(1.63), 320(2.0), 319(2.18), 305(0.66), 289(1.0), 248(1.9), 247(7.09), 246(1.09), 245(1.27), 207(1.63), 205(1.45), 180(1.63), 175(1.63), 167(1.63), 165(0.66), 163(1.8), 161(1.0), 149(2.54), 147(2.18), 135(4.54), 133(5.00), 121(3.81), 119(3.45), 111(10.0), 110(100; C₇H₁₀O), 109(8.0), 108(4.54), 107(6.72), 105(5.27), 95(7.09), 93(7.0), 91(5.45), 83(4.36), 81(1.72), 79(5.45), 68(12.54), 57(5.45), 55(5.45), 43(7.45), 41(6.36).

5-Keto-4,5-secocholestan-4-oic acid (CXX)

M⁺ 418(2.00; C₂₇H₄₆O₃), m/e 403(2.00), 400(5.26), 385(5.26), 332(80.26), 317(7.2), 314(4.0), 247(13.1), 231(11.8), 230(12.0), 229(11.8), 201(11.8), 177(12.5), 173(10.0), 163(13.1), 161(18.4), 159(15.8), 149(21.05), 147(31.58), 145(25.00), 135(39.47), 133(31.58), 121(34.2), 119(27.6), 112(81.5), 108(84.2), 95(64.3), 93(52.62), 91(31.58), 83(43.42), 81(71.5), 79(44.71), 71(39.4), 69(69.7), 67(54.0), 60(15.8), 57(81.5), 55(100), 43(98.68), 41(77.6).
6-Oxa-B-homocholest-4-en-7-one (CXIII)

M⁺ 400 (18.0; C₂₇H₄₄O₂), m/e 385 (9.0), 372 (92.8),
357 (25.0), 354 (15.76), 330 (69.64), 289 (7.14), 287 (7.14),
275 (10.71), 259 (14.3), 247 (24.1), 240 (12.5), 230 (5.35),
217 (14.3), 215 (10.7), 201 (7.14), 193 (8.9), 175 (15.76),
163 (15.76), 151 (15.76), 149 (21.4), 147 (28.57), 136 (42.85),
134 (32.14), 125 (57.14), 122 (32.14), 112 (39.28), 111 (94.64),
110 (26.8), 109 (26.8), 107 (44.64), 95 (75.0), 93 (57.14),
91 (21.4), 81 (64.30), 79 (60.71), 69 (51.8), 67 (46.43), 57 (64.3),
55 (100), 43 (98.21), 41 (80.35).

3β-Acetoxy-6-oxa-B-homocholest-4-en-7-one (XCIX)

M⁺ 458 (10.51; C₂₉H₄₆O₄), m/e 416 (4.6), 399 (11.84),
398 (15.3), 383 (6.58), 371 (17.1), 370 (52.63), 354 (5.26),
330 (9.21), 285 (5.26), 265 (5.26), 247 (22.36), 231 (5.26),
217 (4.6), 191 (7.9), 175 (11.84), 163 (9.21), 161 (7.9), 149 (30.26),
147 (15.8), 135 (39.47), 133 (17.1), 126 (27.63), 123 (15.9),
121 (25.00), 119 (15.8), 111 (25.00), 110 (100), 109 (94.7),
108 (52.65), 107 (35.52), 105 (26.31), 97 (19.73), 95 (52.63),
93 (50.00), 91 (25.0), 83 (31.58), 81 (68.41), 79 (30.26), 71 (43.42),
69 (56.52), 67 (31.58), 60 (32.9), 57 (90.8), 55 (97.4), 43 (100),
41 (80.0).
Methyl 5a-oxa-5-keto-5,6-seco-A-homocholestan-6-oate (CCCI)

\[ M^+ 448(11.3; \text{C}_{28}H_{48}O_4), m/e 433(37.3), 430(5.45), \\
420(19.1), 417(21.81), 416(9.1), 402(6.36), 401(4.1), 363(5.45), \\
335(7.27), 289(10.0), 247(17.27), 233(10.91), 231(10.0), \\
193(8.1), 191(5.7), 174(9.1), 149(12.1), 147(7.0), 128(5.45), \\
127(100; \text{C}_{11}H_{10}O_2), 126(9.1), 121(2.72), 119(10.0), 101(13.63), \\
105(9.1), 95(17.27), 93(10.91), 83(9.1), 81(16.36), 57(21.81), \\
55(23.63). \]

Methyl 5-oxa-6-keto-4,5-seco-B-homocholestan-4-oate (CCCVI)

\[ M^+ 448(10.0; \text{C}_{28}H_{48}O_4), m/e 433(25.8), 431(4.1), \\
420(9.4), 417(12.94), 416(4.7), 402(7.0), 401(4.7), 347(100; \\
\text{C}_{23}H_{39}O_2), 355(5.88), 332(14.0), 247(7.0), 233(7.0), 231(5.88), \\
207(8.23), 205(5.88), 187(15.29), 185(10.0), 165(11.76), \\
163(7.64), 149(10.59), 147(7.06), 145(8.23), 135(18.8), 133 \\
(11.76), 119(10.0), 109(10.4), 107(10.1), 97(8.7), 95(20.0), \\
93(11.7), 57(20.23), 55(25.8), 43(35.17). \]
Methyl 6-oxa-5-keto-4,5-seco-B-homocholestan-4-oate (CCCVIII)

$M^+ \ 448(12.85; \text{C}_{28}H_{48}O_4), \ m/e \ 433(10.0), \ 430(10.0), \ 420(15.5), \ 417(24.28), \ 416(6.0), \ 402(14.2), \ 401(6.0), \ 363(8.57), \ 348(21.42), \ 335(11.4), \ 263(8.57), \ 247(11.42), \ 245(7.1), \ 235(12.85), \ 207(10.0), \ 185(14.28), \ 183(10.0), \ 109(34.28), \ 107(27.1), \ 97(30.0), \ 95(72.86), \ 83(22.85), \ 81(15.71), \ 65(57.1), \ 63(30.0), \ 61(25.71), \ 57(54.28), \ 55(87.1), \ 43(100).$