Lactones\(^1\), resulting from intramolecular acylation of alcohol function of the hydroxy acid by the carboxyl group, are cyclic esters. The ease of formation and breaking of the lactone ring shows remarkably variations with the change in the ring size and the degree of substitution on the ring carbon atoms. In general 5-membered rings are the most stable.

Lactones strictly speaking are heterocyclic ring compound viz. 2-oxo-oxetan or \(^\beta\)-butyrolactone (I), 2-oxooxolan or \(^\gamma\)-bytyrolactone (II) and 2-oxo-oxane, \(^\delta\)-valerolactone (III) or \(^\varepsilon\)-lactone (IV) but they are more usually named after the parent acid. The same Greek letter prefix is used to denote the ring size as that used for the position of the hydroxyl group relating to the carboxyl function in the hydroxy acid. Thus \(^\gamma\)-lactones have 5-membered rings and on hydrolysis, give \(^\gamma\)- or 4-hydroxy acids.
A number of naturally occurring substances having an unsaturated lactone moiety such as protoanemonin, penicillic acid, clavocin and crepin manifest antibiotic action by showing strong antibiotic activities against both gram positive and gram negative bacteria. One of the such simplest substances is protoanemonin isolated from buttercup by Asahina and Fujita\(^2\) first of all and then Anemone pulsatilla by Baer et al.\(^3\). Bear et al. have also investigated the relationship of the structure of simple unsubstituted \(\gamma\)-lactones to antibacterial activities. The discovery of pronounced biological properties\(^4-7\) has boosted the interest in the simple unsaturated lactones which can be regarded as hyroxy derivatives of furans. A few selective examples are being reported here.

The oxidation of organic compounds by Mn (III) complexes in aqueous solutions has been extensively studied and most of the results have been interpreted by inner sphere one-electron transfer process\(^8\).

The oxidation of olefins with lead tetra acetate and other metal complexes has been widely studied\(^8\), but oxidation of olefins with Mn (III) acetate is known to be very little. Heiba et al.\(^9\) reported that Mn (III) acetate, a readily accessible reagent\(^10\), is very much reactive with olefins by a fee radical path way leading to \(\gamma\)-butyrolactones in excellent yields and reported that the oxidation of
octene-1 (V) and trans-stilbene (VI) with Mn (III) acetate in acetic acid and acetic anhydride provided the corresponding γ-lactones (VII) and (VIII).

\[
\begin{align*}
\text{(V)} & \quad \text{CH}_3-(\text{CH}_2)_5-\text{CH} = \text{CH}_2 \\
\text{(VII)} & \quad \text{CH}_3-(\text{CH}_2)_5-\text{C} - \text{CH}_2 \\
\text{(VI)} & \quad \text{C}_6\text{H}_5-\text{CH} = \text{CHC}_6\text{H}_5 \\
\text{(VII)} & \quad \text{H}_5\text{C}_6-\text{C} - \text{C}_6\text{H}_5
\end{align*}
\]

The yields were calculated on the basis of Mn$^{+3}$ consumed and proposed a mechanism for the formation of γ-lactones in the similar way as suggested for the lactones obtained from lead (IV) acetate reactions$^{11}$. The difference was only this that the carbomethyl radical was produced directly by the thermolysis of the manganic complex. The better yield of the lactone showed that the carboxymethyl radical added to the olefin faster than
that of oxidation by $\text{Mn}^{+3}$. The side product of the reaction was the allylic acetate produced by the abstraction of an allylic hydrogen by the carboxymethyl radical.

The alkene (IX) on treatment with the solution of $\text{Mn}$ (III) acetate dihydrated in glacial acetic acid provided $\gamma$-lactone (X)$^{12}$. The product so formed was explained by the interaction of the substrate with an electrophile derived from acetate group co-ordinated with the metal (Mn) or from acetic acid.

\[ \text{H}_3\text{C-C=CH}_2 \]

(IX)

\[ \text{H}_3\text{C-C}\bigg\vert\text{C} = \bigg\vert\text{O} \]

(X)

The rate of the reaction was found to be enhanced by the addition of acetic anhydride$^{12}$ but the yield was poor. Although, acetic anhydride did not have direct relationship with the rate of the reaction.

The thermal decomposition studies of ceric and manganic acetate$^{13-15}$ had demonstrated the role of carboxymethyl radical leading to the proposal of free radical
mechanism as illustrated below:

The general reaction in the synthesis of \( \gamma \)-lactones consisted of the addition of a carboxylic acid with \( \alpha \)-hydrogen atom, across the double bond in the presence of stoichiometric amount of various metal oxidants. The olefins such as 2-methyl propene-1 (XI), hexadiene-1,5 (XII), octadiene-1,7 (XIII) butadiene (XIV) and isoprene (XV) were treated with Mn (III) acetate in presence of acetic acid and acetic anhydride and the formation of respective lactones (XVI), (XVII), (XVIII), (XIX), (XX) & (XXI) were reported\(^\text{15}\).
CH = CH, \(\text{CH}^2\)

\((\text{XI})\)

\(\text{H}_2\text{C} = \text{CHCH}_2 - \text{CH}_2 - \text{CH} = \text{CH}_2\)

\((\text{XII})\)

\(\text{H}_2\text{C} = \text{CH(CH}_2)_4 - \text{CH} = \text{CH}_2\)

\((\text{XIII})\)

\(\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2\)

\((\text{XIV})\)

\(\text{CH}_3\)

\(\text{CH}_2 = \text{CH} - \text{C} = \text{CH}_2\)

\((\text{XV})\)

\(\text{CH}_2 = \text{CH} - (\text{CH}_2)_4\)

\((\text{XVI})\)

\(\text{CH}_2 = \text{CH}(\text{CH}_2)_4 - \text{CH} = \text{CH}_2\)

\((\text{XVII})\)

\(\text{CH}_2 = \text{CH}- (\text{CH}_2)_4\)

\((\text{XVIII})\)

\(\text{CH}_2 = \text{CH}\)

\((\text{XIX})\)

\(\text{CH}_2 = \text{CH}\)

\((\text{XX})\)

\(\text{CH}_3\)

\(\text{CH}_2 = \text{CH}- (\text{CH}_2)_4\)

\((\text{XXI})\)
The oxidation of benzofuran (XXII) with Mn (III) acetate in a mixture of acetic acid and acetic anhydride mainly provided 3a,8b-dihydrofuro(3,2b)benzofuran-2(3H-one) (XXIII).\(^1\)

Osman and Coworkers\(^2\) reported that the oxidation of 10-undecenoic acid (XXIV) with Mn (III) acetate yielded mainly 5-(w-carboxy octyl)γ-butyrolactone (XXV).

\[
\text{CH}_2 = \text{CH-} (\text{CH}_2)_g \text{COOH}
\]

\[(\text{XXIV})\]

\[
\text{CH}_2 = \text{CH-} (\text{CH}_2)_g \text{COOH}
\]

\[(\text{XXV})\]

Okano\(^3\) reported the oxidation of 2-methyl-2-pentene (XXVI) and 1-hexene (XXXI) with Mn (III) acetate in presence of acetic acid, 2-methyl-2-pentene (XXVI) gave 4-acetoxy-3-ethyl-4-methyl pentanoic acid (XXVII), γ-lactone of 3-ethyl-4-hydroxy-4-methyl pentanoic acid (XXVIII), 3-isopropenyl pentanoic acid (XXIX) and 3-ethyl-4-methylene heptanedioic acid (XXX). 1-Hexene (XXXI) yielded 3-octenoic acid (XXXII). 4-octenoic acid (XXXIII), octanoic acid (XXXIV), the
\( \gamma \)-lactone of 4-acetoxy octanoic acid (XXXV) and 4-acetoxy octanoic acid (XXXVI).

\[
\begin{align*}
\text{(XXV)} & \quad \text{CH}_3 - \text{CH}_2 - \text{CH} = \text{C} - \text{CH}_3; \\
\text{(XXVI)} & \quad \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{C} - \text{CH}_3 \\
\text{(XXVII)} & \quad \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{C} = \text{CH}_2 - \text{COOH} \\
\text{(XXVIII)} & \quad \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{C} - \text{CH}_3 \\
\text{(XXIX)} & \quad \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{C} = \text{CH}_2 - \text{COOH} \\
\text{(XXX)} & \quad \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{C} - \text{CH}_2 - \text{COOH} \\
\text{(XXXI)} & \quad \text{CH}_3 - (\text{CH}_2)_3 - \text{CH} = \text{CH}_2; \\
\text{(XXXII)} & \quad \text{CH}_3 - (\text{CH}_2)_3 - \text{CH} = \text{CH} - \text{CH}_2 - \text{COOH} \\
\text{(XXXIII)} & \quad \text{CH}_3 - (\text{CH}_2)_2 - \text{CH} = \text{CH} - (\text{CH}_2)_2 - \text{COOH} \\
\text{(XXXIV)} & \quad \text{CH}_3 - (\text{CH}_2)_6 - \text{COOH} \\
\text{(XXXV)} & \quad \text{CH}_3 - (\text{CH}_2)_3 - \text{COOH} \\
\text{(XXXVI)} & \quad \text{CH}_3 - (\text{CH}_2)_3 - \text{CH} - (\text{CH}_2)_2 - \text{COOH} \\
\end{align*}
\]
In 1980, α-phenylcinnamic acid (XXXVII) was reported to yield spirolactone (XXXVIII) and 5-acetoxy-4, 5-diphenyl-2(5H)-furanone (XXXIX) by the oxidation of Mn(III) acetate in presence of acetic acid and acetic anhydride.

\[
\text{H}_5\text{C}_6\text{-CH} = \text{C} \quad \begin{array}{c}
\text{COOH} \\
\text{C}_6\text{H}_5
\end{array}
\]

(XXXVII)

(XXXVIII)

(XXXIX)

In 1985, Nishino reported that 1,1-diphenyl ethene (XL) on oxidation with the same reagent i.e. Mn(III) acetate in presence of malonamide (XLI) gave 2-carbamoyl-4, 4-diphenyl-2-buten-4-olide (XLII), 3,3,8,8-tetraphenyl-2, 7-dioxaspiro(4,4) nonate-1,6-dione (XLIII) and benzophenone (XLIV).

\[
\begin{array}{c}
\text{CH}_2(\text{CONH}_2)_2 \\
\text{C} = \text{CH}_2
\end{array}
\]

(XLI)

(XL)

(XLII)

(XLIII)

(XLIV)
Nishino\textsuperscript{20} also reported the oxidation of 1,1-bis(4-methoxyphenyl)ethene (XLV) under similar reaction conditions and isolated $\alpha,\beta$-unsaturated-$\gamma$-lactams e.g. 3-carbamoyl-5,5-bis(4-methoxy phenyl) 1H-pyrol-2(5H)-one (XLVI) and 3-carbamoyl-4-hydroxy-5,5-bis(4-methoxyphenyl) 1H-pyrrol-2(5H)-one (XLVII) instead of corresponding 2-buten-4-olide (XLVIII).

Fristad and Peterson\textsuperscript{21} reported the oxidation of various olefins e.g. cis-octene-4(XLIX), trans-octene-4
(LII), cyclohexene (LIII) and cycloheptene (LVI) with Mn(III) acetate in acetic acid and potassium acetate and isolated the corresponding isomeric $\gamma$-lactones namely tran-dihydro-4,5-dipropyl-2(3H)-furanone (L), cis-dihydro-4,5-dipropyl-2(3H)furanone (LI), transhexahydro-2(3H)-benzofuranone (LIV), cis-hexahydro-2(3H)-benzofuranone (LV), trans-octahydro-2H-cyclohepta(b)furan-2-one (LVII) and cis-octahydro-2H-cyclohepta(b)-furan-2-one (LVIII).
Ahmad et al.\textsuperscript{22,23} reported the synthesis of \( \gamma \)-lactones in the cholestane and stigmastane series using \( \alpha,\beta \)-unsaturated ketones, and olefins with Mn (III) acetate and suggested the mechanism for the formation of lactone and other side products. They reported that cholest-3,5-dien-7-one (LIX) on reaction with Mn (III) acetate in presence of acetic acid and acetic anhydride afforded 4\( \beta \)-hydroxy-7-oxocholest-5-en-3\( \beta \)-yl acetic acid \( \gamma \)-lactone (LX).

\[ \text{(LIX)} \]

\( 3\beta \)-Chlorocholest-5-en-7-one (LXI) and \( 3\beta \)-acetoxy cholest-5-en-7-one (LXII) on the similar treatment provided the same lactone (LX).

\[ \text{(LXI)} \]

\[ \text{(LXII)} \]
3β-Chloro stigmast-5-ene (LXIII) and 3β-acetoxy stigmast-5-ene (LXIV) provided 7α-acetoxy-3α-hydroxystigmast-5-en-4β-yl acetic acid γ-lactone (LXV).  

![Chemical Structures](attachment:image.png)

The transformation of the carbonyl compounds into esters by peroxo compounds was known as Baeyer-Villiger oxidation in which the carbon-carbon bond (adjacent to the carbonyl group) cleavage took place with the insertion of the oxygen atom. Thus, the open chain ketones were changed into esters whereas the cyclic ketones afforded the corresponding lactones. In 1899 Baeyer and Villiger reported the oxidation of ketones with the help of Caro's acid (Peroxy sulfuric acid). The other principal peroxo acids which came into the use were peroxo acetic acid, trifluoroacetic acid, perbenzoic acid, metachloroperbenzoic acid and monoperphthalic acid.

Gardner and Godden reported that 5β-cholestan-3-one (LXVI) on heating with ammonium persulfate and acetic acid produced 4-oxa-A-homo-5β-cholestan-3-one (LXVII).
Ellis and Gardner oxidised 5α-cholestan-3-one (LXVII) with ammonium persulfate and aqueous acetic acid and reported two isomeric lactones, 4-oxa-A-homo-5α-cholestan-3-one (LXVIII) and 3-oxa-A-homo-5α-cholestan-3-one (LXIX).

Fonken and Miles showed that 5α-cholestan-6-one (LXX) and 3β-acetoxy-5α-cholestan-6-one (LXXI) on treatment with perbenzoic acid gave corresponding 6-oxa lactones (LXXII) and (LXXIII).
Ahmad et al. observed that 3β-acetoxy-5α-sitostan-6-one (LXXIV) on oxidation with perbenzoic acid afforded the expected 6-oxa lactone (LXXV) as well as the isomeric 7-oxa lactone (LXXVI) which was totally unexpected in the view that Baeyer-Villiger oxidation of 6-ketosteroids was a stereospecific process leading to entirely the 6-oxa steroids by superior migration of a more substituted C\textsubscript{5} relative to C\textsubscript{7}. 
Recently, Baeyer-Villiger oxidation of ketones was carried by using molecular oxygen and benzaldehyde. In this system, perbenzoic acid was produced in situ and the peracid so formed oxidised the ketones to provide the lactones or esters.

(LXXXIII)  (LXXXIV)

(LXXXV)  (LXXXVI)

(LXXXVII)  (LXXXVIII)

(LXXXIX)  (XC)
DISCUSSION

The oxidation of olefins with the easily accessible metal salts like lead tetra acetate and manganese triacetate known for multiplicity of products has been extensively studied mainly in the acyclic systems. A little attempts were made in the steroidal systems.²²,²³

The synthesis of γ-lactone moiety had attracted the much interest²⁴ because of its occurrence in a wide variety of natural compounds having considerable biological activities such as growth inhibitor⁵, allergenic⁶, antibacterial³² and antitumor agents.³³-³⁵

Scheme

\[
\text{Scheme}
\]

\[
\text{HO} \quad \text{Ac}_2\text{O/Py} \quad \text{AcO} \quad \text{HCl} \quad \text{Amyl Alcohol} \quad \text{Mn(III) Acetate}
\]

(LXXVII) \quad (LXXVIII) \quad (LXXXII)
The oxidation of the steroidal olefins by the metal salt $[\text{Mn}(\text{III}) \ \text{acetate}]$ provided the $\gamma$-lactones. The mechanism for the formation of the $\gamma$-lactones was assigned as below.$^{36}$

To judge the validity of the above mechanism, the diene (LXXXII) of the cholestane series was synthesised first of all and then treated with the manganic salt $[\text{Mn}(\text{III}) \ \text{acetate}]$ to afford $7\alpha$-acetoxy-4$\beta$-hydroxycholest-5-en-3$\beta$-yl acetic acid $\gamma$-lactone (LXIX), 7$\alpha$-acetoxy-3
α-hydroxycholest-5-en-4α-yl acetic acid γ-lactone (LXX) and 6β-carboxy methylene 4β,5-dihydroxy-5α-cholest-3β-yl acetic acid γ-lactone (LXXI).

Pyrolytic reaction of 3β-acetoxycholest-5-ene (LXXVIII) with HCl in refluxing amyl alcohol:

A mixture of 3β-acetoxy cholest-5-ene (LXXVIII), amyl alcohol and HCl were refluxed for 3 hours. The contents were washed with water sodium bicarbonate solution and water. Alcohol was removed under reduced pressure and the residue was chromatographed providing crystallisable solid having m.p. 78.5-79.5°C.

Characterisation of the compound, m.p. 78.5-79.5°C, as cholest-3,5-diene (LXXXII):

The elemental analysis of the compound with m.p. 78.5-79.5°C gave a molecular formula corresponding to C_{27}H_{44}. The U.V. spectrum provided λmax at 236 nm, IR of the compound showed a band at 1605 cm\(^{-1}\) for (C=C). The \(^1\)H-NMR revealed a multiplet centred at \(δ\) 5.87 for 1-proton at C\(_6\), another multiplet centred at \(δ\) 5.59 again for 1-proton was assigned for C\(^v\) vinyl proton. The peak at \(δ\) 5.41 as a doublet integrating for 1-proton was assigned for C\(_4\) proton. The angular methyl protons appeared at \(δ\) 1.15 and 0.70 for C\(_{10}\)-CH\(_3\) and C\(_{13}\)-CH\(_3\) respectively while the side chain methyl...
protons appeared at 0.95, 0.90 and 0.80. The mass spectrum of the compound gave molecular ion peak at m/z 368 in 100% relative abundance. So, on the basis of above discussion, the compound was characterised as cholest-3,5-diene. The some of the important fragment ions in mass spectrum are given below:

**Mass fragment peaks**

![Mass Fragment Peaks Diagram](image)
Reaction of cholest-3,5-diene (LXXXII) with manganese triacetate:

Cholest-3,5-diene was subjected to manganese triacetate oxidation in acetic acid and acetic anhydride. After completion of the reaction, the contents were worked up in ether by washing the ethereal solution with water, sodium bicarbonate solution (5%) and water. After column chromatography, these products were obtained as a crystallisable solid with m.p. 69-70°C, an oil and a glassy solid.

(LXXXII)

(LXXIX)

(LXXX)
Characterisation of the compound, m.p. 69-70°C, as 7α-acetoxy-4β-hydroxycholest-5-en-3β-yl acetic acid γ-lactone (LXXIX):

The compound analysed for C₃₁H₄₈O₄ showed absorption bands at 1770, 1730, 1640 and 1155 cm⁻¹ for γ-lactone, acetate, C=C, and C-O-groups. Its ¹H-NMR displayed a doublet at δ 6.25 attributed to C₆-vinylic proton. A multiplet centred at δ 5.3 with coupling constant 4 Hz for 1-proton was assigned to C₇-β-proton (equatorial) while the another doublet at δ 5.15 again for 1-proton with coupling constant 5 Hz was given to C₄-α-proton (equatorial). A broad peak at δ 2.5 for 2-protons was assigned to methylene protons of γ-lactone moiety. The singlet at δ 2.1 for 3-protons was due to the methyl protons of acetate group at C₇. The angular methyl protons appeared at δ 1.22 and 0.7 for C₁₀-CH₃ and C₁₃-CH₃ while the side chain methyl protons appeared between δ 0.92 and 0.81. So on the basis of this discussion the structure was concluded as 7α-acetoxy-4β-hydroxycholest-5-en-3β-yl acetic acid γ-lactone (LXXIX).
Characterisation of the oily compound as $7\alpha$-acetoxy-$3\alpha$-hydroxycholest-5-en-4$\alpha$-yl acetic acid $\gamma$-lactone (LXXX):

The elemental analysis of the oily compound could help to provide the molecular formula $C_{31}H_{48}O_4$. The IR of the compound showed the strong absorption bands at 1775 cm$^{-1}$ for C=O of $\gamma$-lactone and 1730 for C=O of CH$_3$COO. The weak absorption band at 1640 cm$^{-1}$ was due to the presence of C=C while another band at 1235 cm$^{-1}$ was again due to the presence of acetate group. The frequency at 1150 cm$^{-1}$ was due to C-O-C linkage. Its $^1$H-NMR gave a doublet at $\delta$ 6.18 for 1 proton, the vinylic proton at $C_6$. A multiplet centred at $\delta$ 5.25 for 1 proton with J-value equal to 4 Hz was because of the proton present at $C_7$ as equatorial proton. Another multiplet centred at $\delta$ 4.71 for 1H with $W_1 = 14$ Hz was assigned to $C_3\alpha$ proton (axial). A broad peak at $\delta$ 2.5 integrating for 2 protons was due to the methylene protons of $\gamma$-lactone. A sharp singlet at $\delta$ 2.1 for three protons was because of the three protons of acetate group at $C_7$. The two singlets each integrating for three protons appeared at $\delta$ 1.19 and 0.70 were assigned to $C_{10}$-CH$_3$ and $C_{13}$-CH$_3$ respectively while the peaks at $\delta$0.93 and 0.81 were due to the presence of side chain methyl protons. So on the basis of above discussion, the oily compound was characterised as $7\alpha$-acetoxy-$3\alpha$-hydroxy-cholest-5-en-4$\alpha$-yl acetic acid $\gamma$-lactone (LXXX).
Characterisation of the glassy solid as 6β-carboxy methylene-4β,5-dihydroxy-5α-cholest-3β γ-l acetic acid γ-lactone (LXXXI)

The compound analysed for C_{31}H_{50}O_{5} showed a broad band at 3300 cm\(^{-1}\) in the IR spectrum for -OH group, another bands at 2700, 1765, 1710 and 1155 cm\(^{-1}\) were for -COOH, γ-lactone C=O, acid carbonyl (-C=O), and C-O-C respectively. The \(^1\)H-NMR of the compound showed an off scale peak at δ 13.4, which disappeared on D\(_2\)O shake was assigned to the proton of acid (COOH), for one proton. A doublet at δ 5.2 with J-value 4 Hz was also for one proton. It was assigned to C\(_4\)α-proton, (equatorial proton). A broad peak at δ 4.7 again disappearing on D\(_2\)O shake was assigned to the hydroxyl group at C\(_5\). A doublet at δ 2.6 for 2 protons with J-value 7 Hz was assigned to methylene protons of carboxy group at C\(_6\). A broad peak at δ 2.4 for 2 protons was due to the presence of methylene group in γ-lactone moiety. The two singlets for 3 protons each at δ 1.26 and 0.72 were for C\(_{10}\)-CH\(_3\) and C\(_{13}\)-CH\(_3\) respectively while side chain methyl protons appeared between δ 0.92 and 0.84. So, on the basis of above discussion, the compound was characterised as 6β-carboxy methylene-4β,5-dihydroxy-5α-cholest-3β γ-l acetic acid γ-lactone (LXXXI).

Baeyer - Villiger oxidation of ketones to yield esters with the help of peracids has been the subject of extensive investigation. Among ketones of a wide variety of
organic compounds were the steroidal ketones at different nuclear positions. A typical procedure of Baeyer - Villiger oxidation of ketones has been adopted here in which the peracid was generated in situ with the help of benzaldehyde and molecular oxygen.  

The steroidal ketones viz., 5\(\alpha\) -cholestan-6-one (XCI), 3\(\beta\)-choro-5\(\alpha\)-cholestan-6-one (XCII) and 3\(\beta\)-acetoxy-5\(\alpha\)-cholestan-6-one (XCIII) were treated with benzaldehyde and molecular oxygen in carbon tetrachloride as a solvent to provide 5\(\beta\)-cholestan-6-one (XCIV), 6-oxa-B-homo-5\(\alpha\)-cholestan-7-one (XCV), 3\(\beta\)-chloro-7-oxa-B-homo-5\(\alpha\)-cholestan-6-one (XCVI) and 3\(\beta\)-hydroxy-5\(\alpha\)-cholestan-6-one (XCVII) as explained in the scheme-1, given on the next page.

**Reaction of 5\(\alpha\)-cholestan-6-one (XCI) with benzaldehyde and molecular oxygen:**

5\(\alpha\)-cholestan-6-one (XCI) was treated with the solution of benzaldehyde in carbon tetrachloride with bubbling of oxygen gas in presence of benzoylchloride (as catalyst). After passing the gas for a period of 8 hours, the solution was washed with sodium sulfite solution (5%), water, sodium bicarbonate solution (5%) and again with water. Dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The oily mass so obtained was column chromatographed over silica gel to afford the two compounds with m.p. 128\(^\circ\)-130\(^\circ\)C and 158\(^\circ\)C.
Scheme - 1

\( \text{LXXXII} \) → (i) \( \text{NaNO}_2/\text{HNO}_3 \) → (ii) \( \text{Zn - AcOH} \) → (XCIII) → \( \text{O}_2/\text{C}_6\text{H}_5\text{CHO} \) → (XCVII)

\( \text{CI} \) → \( \text{ACO} \)

\( \text{XCVI} \) → \( \text{Cl} \)

\( \text{XCII} \) → (i) \( \text{NaNO}_2/\text{HNO}_3 \) → (ii) \( \text{Zn - AcOH} \) → (XCIX) → (XC)

\( \text{O}_2/\text{C}_6\text{H}_5\text{CHO} \) → (XCIII)

\( \text{Cl} \)

\( \text{XCII} \) → (i) \( \text{NaNO}_2/\text{HNO}_3 \) → (ii) \( \text{Zn - AcOH} \) → (XCIII) → (XCV) + (XCVI)
Characterisation of the compound, m.p. 128-130°C as 5β-cholestan-6-one (XCV):

The elemental analysis of the compound proved the molecular formula as C_{27}H_{46}O. In its IR, a very strong band at 1700 cm\(^{-1}\) was seen for carbonyl group. In \(^1\)H-NMR, three protons of C\(_5\) and C\(_7\) bunched together at \(\delta\) 2.158 as an unequal doublet and a septet for three protons of C\(_4\) and C\(_8\) appeared at \(\delta\) 2.026 with coupling constant 12 Hz. The methyl protons of C\(_{21}\) appeared as a doublet at \(\delta\) 0.916 with coupling constant 6.5 Hz. The protons of C\(_{26}\) and C\(_{27}\) appeared as doublet again at \(\delta\) 0.864 and 0.862 with coupling constant 6.5 Hz. The angular methyl protons appeared as singlet at \(\delta\) 0.824 for C\(_{19}\) protons and \(\delta\) 0.645 for C\(_{18}\) protons. In \(^13\)C-NMR, the carbonyl carbon appeared at \(\delta\) 215.754 and the methine carbon C\(_5\) at \(\delta\) 61.132. In mass spectrum the molecular ion peak along with the proton of matrix appeared as (M+H)^+
at m/z 387. In chemically ionized mass spectrum the peak at m/z 409, molecular ion along with sodium, was as (M+Na)$^+$. So, on the basis of these facts, the compound, m.p. 128-130°C was characterised as 5β-cholestan-6-one. The formation of some of the fragment ions is given in the scheme-2.

![Scheme 2](attachment:image.png)
Characterisation of the compound, m.p. 158°C, as 6-oxa-B-homo-5α-cholestan-7-one (XCV):

The elemental analysis of the compound proved the molecular formula as $\text{C}_{27}\text{H}_{46}\text{O}_2$. In the IR spectrum, a strong band at 1715 cm$^{-1}$ was observed which was due to the presence of $\varepsilon$-lactone moiety. The band at 1270 cm$^{-1}$ was medium which was for the C-O linkage. In $^1\text{H}$-NMR, a double doublet at $\delta$ 4.17 for one proton with coupling constants 11 Hz and 5.5 Hz was observed proving the orientation of C$_5$ as $\alpha$-H. The two double doublets were seen at $\delta$ 2.51 and $\delta$ 2.40 with coupling constants 13.5 Hz and 1.5 Hz each integrating for one proton. These were due to the presence of C$_7$ protons. The coupling constant values for these two protons suggested that neither of the proton was axial nor equatorial. The methyl protons of C$_{21}$ appeared as doublet with coupling constant 6.5 Hz at $\delta$ 0.888. The protons of C$_{19}$ appeared as singlet at $\delta$ 0.886. The other side chain methyl protons i.e. the protons of C$_{26}$ and C$_{27}$ appeared as doublets with J-value 6.5 Hz at $\delta$ 0.861 and $\delta$ 0.860. The angular methyl protons of C$_{18}$ appeared at $\delta$ 0.680 as singlet. In $^{13}\text{C}$-NMR, a peak at $\delta$ 175.152 was observed which was due to the presence of carbonyl carbon but the high field value for the carbonyl carbon suggested that the carbonyl group was not free but in the form of ester carbonyl. Another peak at $\delta$ 83.864 was observed which was assigned to C-5 attached.
with the oxygen atom of the lactone moiety. In the mass spectrum a peak at m/z 403 for (M+H)^+ and a peak at m/z 425 for (M+Na)^+ were observed. Some of the important fragment ion peaks had been rationalised in scheme 3. So on the basis of above evidences, structure for the compound was suggested as 6-oxa-B-homo-5α-cholestan-7-one (XCV). The structure was further confirmed by X-ray.

**Scheme 3**

- M+Na^+ m/z 425
- (M+H^+) m/z 403
- H_2O, m/z 385
- CH_2=CH=O, m/z 343
- C_20H_36O_2, m/z 95

\[ \text{[M+Na]^+ m/z 425} \]
Reaction of $3\beta$-chloro-$5\alpha$-cholestan-6-one (XCII) with benzaldehyde and molecular oxygen:

$3\beta$-Chloro-$5\alpha$-cholestan-6-one (XCII) was treated in the similar fashion as $5\alpha$-cholestan-6-one (XCI) with benzaldehyde and molecular oxygen. After work up and column chromatography, the compound, m.p. 146°C was obtained along with the starting ketone (XCII).

Characterisation of the compound, m.p. 130°C, as $3\beta$-chloro $5\alpha$-cholestan-6-one (XCII):

The elemental analysis of the compound supported the molecular formula of the compound, m.p. 130°C as $C_{27}H_{45}OCl$. In IR, strong absorption band at 1715 cm$^{-1}$ was observed which was due to the carbonyl group. A band at 740 cm$^{-1}$ was also seen for C-Cl bond. The $^1$H-NMR of the compound exhibited a peak splitting into nine at $\delta$ 3.794 for one proton with coupling constant 12 Hz giving the orientation as axial to the proton. A double doublet for one proton at $\delta$ 2.316 with
coupling constants 4.5 Hz (axial-equatorial) and 13 Hz (gem coupling) for C-7 (equatorial) was seen. Another double doublet at $\delta$ 2.216 for one proton of C-5 with coupling constants 4.5 Hz and 13 Hz was observed. The C-5 proton appeared in the up field region than the C-7 (equatorial) proton suggested that the C-7 (equatorial) proton was in the carbonyl cone while the C-5 proton was away from the carbonyl group resulting thereby appearing in the higher field than the equatorial proton of C-7. The C-7 axial proton appeared as a triplet with coupling constant 13 Hz at $\delta$ 1.986. The value 13 Hz suggested that the proton at C-8 and another proton at C-7 (equatorial) were behaving like equivalent protons. The methyl protons of the side chain appeared as doublets at $\delta$ 0.902, 0.860 and 0.858 (with J-values 6.5 Hz for each doublets) for C_21, C_26 and C_27 respectively. The angular methyl protons appeared as singlets at $\delta$ 0.779 and 0.657 for C_19 and C_18 respectively. The $^{13}$C-NMR displayed a peak at $\delta$ 209.903 a peculiar characteristic for carbonyl group. In mass spectrometry, the (M+H)$^+$ at m/z 443/445, the peak (2M+2H)$^+$ at m/z 842 were seen. So, on the basis of these findings, the compound was characterised as 3$\beta$-chloro-5$\alpha$-cholestan-6-one. Some of the important fragment ions had been rationalized in the scheme-4.
Scheme - 4

(M+H)^+ \rightarrow \text{m/z} 385

\rightarrow \text{m/z} 367

\text{H}_2\text{O}

\text{HCl}

\text{H}^+(\text{from NBA})

\text{M}^+ 420/422

(Cl)
Characterisation of the compound, m.p. 146°C as 3β-chloro-7-oxa-B-homo-5α-cholestan-6-one (XCVII):

The compound m.p. 146°C was analysed for C_{27}H_{45}O_{2}Cl. Its IR showed band at 1720 cm\(^{-1}\) for carbonyl frequency of \(\varepsilon\)-lactone. A band at 740 cm\(^{-1}\) for C-Cl was also observed. The \(^1\)H-NMR showed a double doublet at \(\delta\) 4.116 for one proton with coupling constants 1.5 Hz and 12 Hz. The peak was assigned to \(\alpha\)-proton of C\(_7\)-attached with the oxygen atom of the lactone moiety. Another proton of C\(_7\) appeared at \(\delta\) 3.972 again as a double doublet with J-values 3 Hz and 12 Hz. A peak as a septet was observed at \(\delta\) 3.768 with J-value 12 Hz. The value 12 Hz suggested the proton at C\(_3\) as axial. The C\(_5\)-proton appeared at \(\delta\) 2.842 as double doublet with coupling constants 4.5 Hz and 12 Hz. These J-values for C\(_5\) suggested that the ring junction A/B was trans. The methyl protons of C\(_{19}\) appeared as singlet at \(\delta\) 0.932. The side chain methyl protons appeared at \(\delta\) 0.900, 0.862 and 0.860 as doublets with J-value 6.5 Hz for C\(_{21}\), C\(_{26}\) and C\(_{27}\). The methyl protons of C\(_{18}\) appeared at \(\delta\) 0.686 as singlet. In mass spectrum, the molecular ion peak along with proton of matrix was observed as (M+H)\(^+\) at m/z 437. So, on the basis of these data, the compound was characterised as 3β-chloro-7-oxa-B-homo-5α-cholestan-6-one (XCVII). The some of the mass fragment ions had been discussed in scheme-5.
Reaction of $3\beta$-acetoxy-$5\alpha$-cholestan-6-one (XCIII) with benzaldehyde and molecular oxygen:

$3\beta$-Acetoxy-$5\alpha$-cholestan-6-one (XCIII) was treated with benzaldehyde and molecular oxygen in the similar fashion as $5\alpha$-cholestan-6-one (XCI) was treated. After usual work up and column chromatography, the compounds m.p. 128°C, 165°C were obtained.
Characterisation of the compound, m.p. 128°C, as 3β-acetoxy-5α-cholestan-6-one(XCIII):

The compound m.p. 128°C was analysed for C_{29}H_{48}O_3. In its IR, bands at 1725 and 1230 cm^{-1} were observed for acetate group while the band at 1710 cm^{-1} was due to the carbonyl group in the steroidal skeleton. The $^1$H-NMR, revealed a peak as septet at $\delta$ 4.666 with coupling constant 12 Hz for C_3-$\alpha$ proton. The equatorial proton of C_7 appeared as a double doublet at $\delta$ 2.312 with J-values 4.5 Hz and 12 Hz for axial-equatorial and gem couplings. The C_5 proton appeared as double doublet at $\delta$ 2.258 with coupling constants 4.5 Hz and 12 Hz. The angular methyl protons appeared at $\delta$ 0.766 and 0.616 as singlet for C_{19} and C_{18} respectively. The side chain methyl protons appeared as doublets at $\delta$ 0.916, 0.862 and 0.860 with J-values 6.5 Hz. In $^{13}$C-NMR, a peak at $\delta$ 210.470 for carbonyl group at C_6 was observed. The another
peak at $\delta$ 170.622 appeared for acetate carbonyl group. The C$_3$-carbon attached with acetate group was seen at $\delta$ 72.847. In mass spectrum, the molecular ion peak at m/z 444 was seen so, on the basis of above discussion, the compound was characterised as 3$\beta$-acetoxy-5$\alpha$-cholestan-6-one (XCIII). Some of the fragment ions had been given in scheme-6.

Characterisation of the compound, m.p. 165°C, as 3$\beta$-hydroxy-5$\alpha$-cholestan-6-one (XCVII):

The compound m.p. 165°C was analysed for C$_{27}$H$_{46}$O$_2$. In its IR, a broad band at 3400 cm$^{-1}$ for hydroxyl group, a band at 1715 cm$^{-1}$ for carbonyl group were observed.
\(^1\text{H-NMR}\), a peak as septet was observed at \(\delta 3.642\) for \(C_3\)-proton with \(J\)-value 12 Hz. The \(J\)-value suggested the \(\alpha\)-orientation of the proton. The equatorial proton of \(C_7\) was observed at \(\delta 2.324\) with coupling constants 4.5 Hz and 13 Hz for axial-equatorial and and gem couplings. The \(C_5\) proton appeared as a double doublet at \(\delta 2.210\) with coupling constants 4.5 Hz and 12 Hz for being axial in nature itself. In \(^{13}\text{C-NMR}\), a peak at \(\delta 210.882\) was observed for carbonyl carbon. The another peak at \(\delta 70.703\) was for \(C_3\)-carbon attached with hydroxyl group. In mass spectrometry, the peak \((\text{M+H})^+\) was observed at \(m/z\) 403. So, on the basis of above discussion, the structure for the compound was concluded as \(3\beta\)-hydroxy-5\(\alpha\)-cholestan-6-one (XCVII). The formation of some of the fragment ions could be concluded as in scheme-7.

![Scheme-7](image-url)
All melting points were observed on a Kofler hot block apparatus and are uncorrected. IR spectra were obtained in KBr unless otherwise specified and the values given are in cm\(^{-1}\). NMR spectra were run in CDCl\(_3\) with Me\(_4\)Si as the internal reference and values are given in ppm (\(\delta\)) (s, singlet; br, broad; d, doublet; dd, double doublet; t, triplet; mc, multiplet centred at). Thin layer chromatographic (TLC) plates were coated with silica gel and sprayed with 20\% aqueous solution of perchloric acid. Petroleum ether refers to a fraction of b.p. 40-60\%. Silica gel (\(\sim\) 20) was used for each gram of the material to be separated in column chromatography. All glass wares were heated in oven at a temperature range of 200-225°C for at least 8 hours prior to their use. The solvents and reagents were purified according to the literature procedure.

Pyrolytic elimination of acetoxy group from 3\(\beta\)-acetoxy-cholest-5-ene (LXXVIII) in presence of HCl in amyl alcohol:

Cholest-3,5-diene (LXXXII):

To a hot solution of 3\(\beta\)-acetoxy cholest-5-ene (LXXVIII, 5g) in amyl alcohol (100 ml), concentrated hydrochloric acid (36\%, 20 ml) was added. The contents were heated under reflux for 3 hours. After a period of 3 hours, the mixture was washed with water, sodium bicarbonate solution (5\%) and water. The amyl alcohol layer was
collected and was evaporated under reduced pressure. The residue so obtained was chromatographed over silica gel. Elution with petroleum ether (40-60°) afforded an oil which was crystallised from a mixture of acetone and ethyl alcohol to give the crystals of diene (LXXXII, 4.1g) m.p. 78.5-79.5°C (reported37 m.p. 80°).

Analysis found : C, 87.84; H, 11.34
Required : C, 88.04; H, 11.41%
U.V. : \( \lambda_{\text{max}} \) 236 nm
IR (Nujol) : \( \nu_{\text{max}} \) 1605 cm\(^{-1}\) (C=C)

\(^1\)H-NMR : \( \delta \) 5.87 (dd, 1H, \( C_6 \)-vinyllic), 5.59 (mc, 1H, \( C_3 \)-vinyllic), 5.41 (d, 1H, \( C_4 \)-vinyllic), 1.15 (s, 3H, \( C_{10} \)-CH\(_3\)), 0.70 (s, 3H, \( C_{13} \)-CH\(_3\)), 0.95, 0.90 and 0.80 (side chain methyl protons).

Reaction of cholest-3,5-diene (LXXXII) with manganese triacetate and acetic anhydride: 7\alpha\text{-}Acetoxy-4\beta\text{-}hydroxy cholest-5-en-3\beta\text{-}yl acetic acid \gamma\text{-}lactone (LXXIX), 7\alpha\text{-}Acetoxy-3\alpha\text{-}hydroxy cholest-5-en-4\alpha\text{-}yl acetic acid \gamma\text{-}lactone (LXXX) and 6\beta\text{-}Carboxy methylene-4\beta,5\text{-}dihydroxy-5\alpha\text{-}cholest-3\beta\text{-}yl acetic acid \gamma\text{-}lactone (LXXXI):

A mixture of cholest-3,5-diene (LXXXII, 2g), manganese triacetate (18g), acetic acid (60 ml) and acetic anhydride (20 ml) was heated under refluxed condition for a period of 2.5 hours and then cooled down to room temperature. The reaction mixture was poured into water and extracted with ether. The ethereal layer was washed with water, sodium bicarbonate solution (5%), water and brine. Dried over anhydrous sodium sulfate and the solvent was evaporated. The evaporation of the solvent provided an oil which was chromatographed over silica gel. Elution with petroleum ether: ether (8:1) provided 7\alpha\text{-}Acetoxy-4\beta\text{-}hydroxycholest-5-en-3\beta\text{-}yl acetic acid \gamma\text{-}lactone (370 mg) crystallised from petroleum ether, m.p. 69-70°C (reported \textsuperscript{36} m.p. 71°C).
Analysis found : C, 76.69; H, 9.78
Required : C, 76.81; H, 9.98%
IR : $\nu_{\text{max}}$ 1770 (γ-lactone C=O), 1730 (CH$_3$COO),
    1640 (C=C), 1235 (CH$_3$COO), 1155 cm$^{-1}$ (C=O).
$^1$H-NMR : $\delta$ 6.25 (d, 1H, C$_6$-vinylic proton), 5.3
    (mc, 1H, C$_7$-$\beta$ H, equatorial, J$_{ax}$=4Hz),
    5.15 (d, 1H, C$_4$-$\alpha$ H, equatorial, J$_{ax}$=5Hz),
    2.5(br, 2H, -CH$_2$-COO, γ-lactone methylene
    protons), 2.1(s, 3H, CH$_3$-COO), 1.22 (s,
    3H, C$_{10}$-CH$_3$), 0.70 (s, 3H, C$_{13}$-CH$_3$), 0.92
    and 0.81 (other side chain methyl
    protons).

Elution with petroleum ether: ether (4:1)
provided 7α-acetoxy-3α-hydroxycholest-5-en-4α-yl acetic acid
γ-lactone (LXXX, 150 mg) a non-crystallisable oily compound.

Analysis found : C, 76.65; H, 9.81
Required : C, 76.81; H, 9.98%
IR (Nujol) : $\nu_{\text{max}}$ 1775 (γ-lactone C=O), 1730 (CH$_3$COO),
    1640 (C=C), 1235 (CH$_3$COO), 1150 cm$^{-1}$ (C=O).
$^1$H-NMR : $\delta$ 6.18 (d, 1H, C$_6$-vinylic proton), 5.25
    (mc, 1H, C$_7$-$\beta$ H, equatorial, W$_h$ = 4Hz),
    4.71 (mc, 1H, C$_3$-$\beta$ H, axial, W$_h$ = 14 Hz),
2.5 (br, 2H, -CH$_2$-COO-; $\gamma$-lactone methylene), 2.1 ($s$, 3H, CH$_3$-COO), 1.19 ($s$, 3H, C$_{10}$-CH$_3$), 0.70 ($s$, 3H, C$_{13}$-CH$_3$), 0.93 and 0.80 (other side chain methyl protons).

Elution with ether provided a non-crystallisable glassy-solid, 6$\beta$-carboxy methylene-4$\beta$, 5-dihydroxy-5$\alpha$-cholest-3$\beta$-yl acetic acid $\gamma$-lactone (LXXXI, 700 mg).

Analysis found : C, 73.5; H, 9.78
Required : C, 74.1; H, 9.96%

IR : $\nu$ max 3300 (br, -OH), 2700 (-COOH), 1765 ($\gamma$-lactone C=O), 1710 ($\gamma$-OH) and 1155 cm$^{-1}$ (C-O).

$^1$H-NMR : $\delta$ 13.4 (br, 1H, COOH, exchangeable with deuterium), 5.2 (d, 1H, C$_4$-$\alpha$H, equatorial, Jae=4Hz), 4.7 (br, 1H, -OH, exchangeable with deuterium), 2.6 (d, 2H, C$_6$-CH$_2$-COOH J=7Hz), 2.4 (br, 2H, -CH$_2$-COO-, $\gamma$-lactone methylene), 1.26 ($s$, 3H, C$_{10}$-CH$_3$), 0.72 ($s$, 3H, C$_{13}$-CH$_3$), 0.92 and 0.84 (other side chain methyl protons).

Cholest-5-ene (XCIX):

3$\beta$-Chlorocholest-5-ene$^{38}$ (15.0g) was dissolved in warm amyl alcohol (300 ml) and sodium metal (35.0g) was
added in small portions over a period of 8 hours. The reaction mixture was heated now and then during the course of reaction so as to keep the sodium metal dissolved. The reaction mixture was poured into water acidified with HCl and allowed to stand over night. A white crystalline solid was obtained which was filtered under suction and washed thoroughly with water and air dried. Recrystallisation of the crude material from acetone gave the desired compound in cubes (10.8g) m.p. 92°C (reported, m.p. 89.5-91.2°C).

6-Nitrocholest-5-ene (C):

A suspension of freshly powdered cholest-5-ene (XCIX, 6.0g) in glacial acetic acid (50 ml) was stirred at room temperature for 10 minutes, fuming nitric acid (20 ml; d, 1.52) was added and sodium nitrite (12.0g) was added in small portions in 1 hour with continued stiring for 2 hours more. The temperature of the reaction mixture was maintained between 20-25°C by external cooling. The reaction mixture was then poured into ice cold water. A yellow solid separated was filtered under suction, washed thoroughly with water and air dried. Recrystallisation from methanol provided pure 6-nitrocholest-5-ene (C 3.5g), m.p. 118°C (reported, m.p. 117-118°C).
5α-Cholestan-6-one (XCI):

6-Nitrocholest-5-ene (C, 6.0 g) was powdered, dissolved in warm glacial acetic acid (120 ml) and zinc dust (12 g) was gradually added with shaking. The suspension was heated for 4 hours and water 12 ml was added during the course of reaction. The hot solution was filtered to remove zinc powder, cooled to room temperature and diluted with excess of water. The precipitate thus obtained was taken in ether. The ethereal solution was washed with water, sodium bicarbonate solution (10%), again with water and dried over anhydrous sodium sulfate. Removal of the solvent provided an oil which on crystallisation from methanol gave thin plates of ketone (XCI, 3.5 g) m.p. 96°C (reported 41, 98°C).

Reaction of 5α-cholestan-6-one (XCI) with benzaldehyde and molecular oxygen in presence of benzoyl chloride (as catalyst): 5β-Cholestan-6-one (XCIV) and 6-oxa-β-homo-5α-cholestan-7-one (XCV):

Into a three necked flask fitted with a reflux condenser cooled at -15°C were placed benzaldehyde (1 ml) and carbon tetrachloride (16 ml), and oxygen was bubbled into the stirred solution at 40°C for 30 minutes. A carbon tetrachloride solution (10 ml) of 5α-cholestan-6-one (XCI, 1.0 g) was added and then benzoyl chloride (.1 ml, catalytic amount) was added. The reaction mixture was cooled to 20°C.
and oxygen was bubbled for a period of 8 hours. After 8 hours, the reaction mixture was worked up by the successive treatment with sodium sulfite solution (5%), water, sodium bicarbonate solution (5%) and again with water and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure gave an oil which was chromatographed over silica gel. Elution with petroleum ether (40-60°) provided an oil which on crystallisation from methanol gave the compound m.p., m.m.p. 96°C same as that of the starting ketone (.4g, XCl). On further elution with petroleum ether : ether (30:1) gave an oil which on crystallisation from ethanol provided a compound (XCV,0.17g) m.p. 128-130°C (reported, m.p. 132°C).

Analysis found : C, 83.71; H, 11.61
Required : C, 83.94; H, 11.92%
IR : \(\nu_{\text{max}}\) 1700 cm\(^{-1}\) (C=O)
\(^1\)H-NMR (CDCl\(_3\)) : \(\delta\) 2.158 (distorted doublet, 3H, C\(_5\) and C\(_7\) protons), 2.026 (septet, 3H, C\(_4\) and C\(_8\) protons, J=12 Hz), 0.916 (d, 3H, C\(_{20}-\text{CH}_3\), J=6.5 Hz), 0.864 (d, 3H, C\(_{25}-\text{CH}_3\), J=6.5 Hz), 0.862 (d, 3H, C\(_{25}-\text{CH}_3\), J=6.5 Hz), 0.824 (s, 3H, C\(_{10}-\text{CH}_3\)), 0.645 (s, 3H, C\(_{13}-\text{CH}_3\)).
$^{13}$C-NMR (CDCl$_3$) : $C_1$(36.038), $C_2$(25.547), $C_3$(24.014), $C_4$
(26.556), $C_5$(61.132), $C_6$(215.754), $C_7$
(43.032), $C_8$(39.967), $C_9$(37.085), $C_{10}$
(38.314), $C_{11}$(20.616), $C_{12}$(39.770),
$C_{13}$(43.032), $C_{14}$(56.201), $C_{15}$(20.889),
$C_{16}$(28.133), $C_{17}$(56.960), $C_{18}$(11.976),
$C_{19}$(24.136), $C_{20}$(35.697), $C_{21}$(18.666),
$C_{22}$(36.114), $C_{23}$(23.809), $C_{24}$(39.474),
$C_{25}$(28.012), $C_{26}$(22.550) and $C_{27}$(22.801)
δ cf43.

Mass : Fast Atom Bombardment (3-Nitro benzyl
alcohol as matrix, gas used-Xe, NaI as
ioniser).

(M+H)$^+$ m/z 387(92), 386(25), 384(32),
383(5), 371(12), 370(13), 369(45),
368(7), 331(12), 273(5), 175(40),
161(39), 159(19), 147(24), 135(48),
109(73), 105(58), 97(38), 95(XX),
93(75), 91(86), 81(XX), 67(100), 66(7),
65(21).

(M+Na)$^+$ m/z 409

(2M+Na)$^+$ 795.

On further elution with pet.ether: ether (20:1) pro-
vided an oily compound which on crystallisation from petroleum
ether gave the crystals (XCV, .3 g), m.p. 158°C (reported
m.p. 155°C).
Analysis found : C, 80.32; H, 11.16
Required : C, 80.6; H, 11.44%
IR : $\nu_{\text{max}}$ 1715 (C=O), 1270 cm$^{-1}$ (C-O)
$^1$H-NMR (CDCl$_3$) : $\delta$ 4.17(dd, 1H, C$_5$-$\alpha$H, Jaa=11 Hz, Jae=5.5 Hz), 2.51(dd, 1H, C$_7$-$\alpha$H, Jgem=13.5 Hz, Jae=1.5 Hz), 2.40(dd, 1H, C$_7$-$\alpha$H, Jgem=13.5 Hz, Jaa=1.5 Hz), .888(d, 3H, C$_{20}$-CH$_3$, J=6.5 Hz), .886(s, 3H, C$_{10}$-CH$_3$), .862(d, 3H, C$_{25}$-CH$_3$, J=6.5 Hz), .860(d, 3H, C$_{25}$-CH$_3$, J=6.5 Hz) and .680(s, 3H, C$_{10}$-CH$_3$).

$^{13}$C-NMR (CDCl$_3$) : C$_1$(29.421), C$_2$(25.317), C$_3$(22.206), C$_4$(39.411), C$_5$-O-(83.864),-C$_6$O-(175.152), C$_7$(39.783), C$_8$(34.92), C$_9$(55.622), C$_{10}$(40.124), C$_{11}$(21.372), C$_{12}$(38.228), C$_{13}$(42.681), C$_{14}$(58.732), C$_{15}$(23.761), C$_{16}$(27.979), C$_{17}$(56.441), C$_{18}$(11.799), C$_{19}$(18.550), C$_{20}$(35.679), C$_{21}$(12.276), C$_{22}$(35.952), C$_{23}$(24.535), C$_{24}$(38.364), C$_{25}$(27.979), C$_{26}$(22.525) and C$_{27}$(22.783)$\delta$ cf 43.

Mass : FAB; NBA and NaI (gas-Xe)
$(M+H)^+$ 403(99), 385(25), 367(7), 344(10), 343(35), 307(7), 289(12), 247(23), 231(8), 193(15), 191(10), 181(10), 175(11),
Reaction of 3β-chloro-5α-cholestan-6-one (XCII) with benzaldehyde and molecular oxygen in presence of benzoyl chloride (as catalyst): 3β-Chloro-7-oxa-B-homo-5α-cholestan-6-one (XCVII):

A solution of 3β-chloro-5α-cholestan-6-one (XCII, 1.1g) was treated with benzaldehyde and molecular oxygen in the similar fashion as 5α-cholestan-6-one (XCI) was treated. After usual work up and column chromatography over silica gel with petroleum ether: ether (25:1) gave a compound m.p. 130°C (reported m.p. 128-129°C).

Analysis found : C, 76.88; H, 10.56
Required : C, 77.14, H, 10.71%
IR : $\nu_{\text{max}}$ 1715 (C=O), 740 cm$^{-1}$ (C-Cl)
$^1$H-NMR (CDCl$_3$) : $\delta$ 3.794 (Nine, 1H, C$_3$-\textit{\textbf{H}}, J=12 Hz), 2.316(dd, 1H, C$_7$-\textit{\textbf{H}}, J$_{gem}$=13 Hz, J$_{aa}$=4.5 Hz), 2.216(dd, 1H, C$_5$-\textit{\textbf{H}}, J$_{ae}$=4.5 Hz, J$_{aa}$=13 Hz), 1.986(t, 1H, C$_7$-\textit{\textbf{H}}, J$_{ae}$=13 Hz, J$_{gem}$=13 Hz), 0.902(d, 3H, C$_{20}$-CH$_3$, J=6.5 Hz), 0.860(dd, 3H, C$_{25}$-CH$_3$, J=6.5 Hz), 0.858(d, 3H, C$_{25}$-CH$_3$, J=6.5 Hz), 0.779 (s, 3H, C$_{10}$-CH$_3$) and 0.657 (s, 3H, C$_{13}$-CH$_3$).

$^{13}$C-NMR (CDCl$_3$) : C$_1$(31.392), C$_2$(32.447), C$_3$(59.005), C$_4$(39.426), C$_5$(58.057), C$_6$=O(209.903), C$_7$(46.632), C$_8$(35.671), C$_9$(53.786), C$_{10}$(40.707), C$_{11}$(21.379), C$_{12}$(38.144), C$_{13}$(42.968), C$_{14}$(56.115), C$_{15}$(23.799), C$_{16}$(28.009), C$_{17}$(56.699), C$_{18}$(12.003), C$_{19}$(13.065), C$_{20}$(37.840), C$_{21}$(18.625), C$_{22}$(36.073), C$_{23}$(23.799), C$_{24}$(39.448), C$_{25}$(27.994), C$_{26}$(22.540) and C$_{27}$(22.797)$\delta$ of 43.

Mass : FAB, NBA (gas used-Xe).

(M+H)$^+$ 423(33), 421(95), 385(25), 367(7), 307(14), 305(10), 265(8), 198(8), 195(11), 160(22), 158(26), 107(100).

(2M+2H)$^+$ as 842.
(M+Na)$^+$ 445(18), 443(55), 423(35), 421 (98), 385(38), 367(16), 160(46), 119 (100).

(M+H+Na)$^+$ as 864.

On continued elution with petroleum ether: ether (16:1) provided an oil which on crystallisation gave the compound (XCVI, 0.25 g), m.p. 146°C (reported, m.p. 145°C).

Analysis found : C, 74.12; H, 10.06

Required : C, 74.31; H, 10.32%

IR : $\gamma_{\text{max}}$ 1720(C=O), 740 cm$^{-1}$ (C-Cl)

$^1$H-NMR (CDCl$_3$) : $\delta$ 4.116(dd, 1H, $C_7$-a$_B$H, J=1.5 Hz and 12 Hz), 3.972(dd, 1H, $C_7$-a$_A$H, J=3 Hz and 12 Hz), 3.768 (septet, 1H, $C_3$-a$_D$H, J=12 Hz), 2.842(dd, 1H, $C_5$-a$_A$H, J$\alpha$=4.5 Hz, J$\alpha_a$=12 Hz), 0.932(s, 3H, $C_{10}$-CH$_3$), 0.900 (d, 3H, $C_{20}$-CH$_3$, J=6.5 Hz), 0.862 (d, 3H, $C_{25}$-CH$_3$, J=6.5 Hz), 0.860 (d, 3H, $C_{25}$-CH$_3$, J=6.5 Hz) and 0.686 (s, 3H, $C_{13}$-CH$_3$).

Mass : 439(16), 437(52), 401(80), 385(23), 367(18), 307(9), 305(11), 289(10), 247 (30), 160(38), 155(82), 150(42), 148 (46), 147(XX), 121(XX), 119(87), 111(65), 109(XX), 107(XX), 97(89),
Reaction of 3β-acetoxy-5α-cholestan-6-one (XCIII) with benzaldehyde and molecular oxygen: 3β-Hydroxy-5α-cholestan-6-one (XCVII):

3β-Acetoxy-5α-cholestan-6-one⁴⁵ (XCIII, 1.1g) was treated with benzaldehyde and molecular oxygen in the similar fashion as 5α-cholestan-6-one (XCI). After usual work up and column chromatography over silica gel and eluting the column with petroleum ether:ether (20:1) gave a compound(XCIII, 0.26g) m.p. 128°C (reported⁴⁵, m.p. 127-128°C).
Hz), .916 (d, 3H, C_{20}-CH_{3}, J=6.5 Hz), .862 (d, 3H, C_{25}-CH_{3}, J=6.5 Hz), .860 (d, 3H, C_{25}-CH_{3}, J=6.5 Hz), .766 (s, 3H, C_{10}-CH_{3}) and .616 (s, C_{13}-CH_{3}).

^{13}C-NMR (CDCl_{3}): \[\begin{array}{c}
\text{C}_1(26.839), \text{C}_2(36.413), (\text{C}_3)(72.847) \\
\text{C}_3-0=\text{C}-\text{CH}_3 (170.622), \text{C}_3-0=\text{C}-\text{CH}_3 (21.362), \\
\text{C}_4(39.470), \text{C}_5(56.485), \text{C}_6=\text{O}(210.470), \\
\text{C}_7(46.669), \text{C}_8(36.086), \text{C}_9(53.837), \text{C}_{10} \\
(40.956), \text{C}_{11}(21.476), \text{C}_{12}(37.945), \text{C}_{13} \\
(42.982), \text{C}_{14}(56.485), \text{C}_{15}(23.972), \text{C}_{16} \\
(28.007), \text{C}_{17}(56.105), \text{C}_{18}(12.024), \text{C}_{19} \\
(13.041), \text{C}_{20}(39.447), \text{C}_{21}(18.639), \text{C}_{22} \\
(26.126), \text{C}_{23}(23.812), \text{C}_{24}(35.699), \text{C}_{25} \\
(28.038), \text{C}_{26}(22.561) \text{ and } \text{C}_{27}(22.819)^{\delta \text{cf}^{43}}.
\end{array}\]

Mass: 445(26), 444(28), 400(27), 386(25), 385(86), 367(18), 271(7), 175(11), 173(9), 161(16), 159(17), 154(19), 149(18), 147(21), 137(36), 121(40), 119(38), 111(11), 109(39), 107(72), 105(55), 95(XX), 93(84), 91(89), 81(100), 79(83), 77(76), 71(52), 69(91), 67(78), 65(17), 63(30), 57(XX), 55(XX), 53(49), 51(26), 50(16). (2M+H)^+889.
(M+Na)$^+$ 467(70), 386(22), 385(76), 367(17), 271(7), 177(9), 176(21), 175(12), 173(9), 161(16), 159(19), 154(20), 137(39), 125(34), 121(45), 119(35), 109(44), 107(85), 105(68), 97(24), 95(XX), 93(97), 91(XX), 89(25), 83(51), 81(XX), 79(100), 75(87), 71(56), 69(XX), 67(92), 57(XX), 55(XX), 53(60), 51(31), 50(16).

On continued elution with the same system i.e. petroleum ether: ether (16:1) gave an oil which on crystallisation from methanol provided a compound (XCVII, 0.31g), m.p. 165°C.

Analysis found : C, 80.39; H, 10.98
Required : C, 80.6; H, 11.44%
IR : $\nu_{\text{max}}$ 3400 (-OH), 1715 cm$^{-1}$ (C=O).
$^1$H-NMR (CDCl$_3$) : $\delta$ 3.642 (septet, 1H, C$_3$-$\alpha$H, J=12 Hz), 2.324 (dd, 1H, C$_7$-$\beta$H, Jae=4.5 Hz, Jgem=13 Hz), 2.210 (dd, 1H, C$_5$-$\alpha$H, Jae=4.5 Hz, Jaa=12 Hz), 0.906 (dd, 3H, C$_{20}$-CH$_3$, J=6.5 Hz), 0.864 (dd, 3H, C$_{25}$-CH$_3$, J=6.5 Hz), 0.862 (dd, 3H, C$_{25}$-CH$_3$, J=6.5 Hz), 0.746 (s, 3H, C$_{10}$-CH$_3$) and 0.660 (s, 3H, C$_{13}$-CH$_3$).
$^{13}$C-NMR (CDCl$_3$) : $C_1(30.703)$, $C_2(30.050)$, $C_3(70.703)$, $C_4 (39.495)$, $C_5(56.745)$, $C_6=O(210.882)$, $C_7(46.724)$, $C_8(37.909)$, $C_9(53.923)$, $C_{10}(40.928)$, $C_{11}(21.516)$, $C_{12}(36.650)$, $C_{13}(42.969)$, $C_{14}(56.768)$, $C_{15}(23.966)$, $C_{16}(38.025)$, $C_{17}(56.123)$, $C_{18}(12.003)$, $C_{19}(13.126)$, $C_{20}(35.678)$, $C_{21}(18.626)$, $C_{22}(36.073)$, $C_{23}(23.799)$, $C_{24}(39.449)$, $C_{25}(27.987)$, $C_{26}(22.533)$ and $C_{27}$ (22.790) $^{3}$cif$^{43}$.

Mass : 403(60), 402(20), 386(26), 385(81), 384(11), 367(35), 289(6), 287(7), 271(10), 261(7), 259(8), 247(14), 219(11), 205(12), 175(28), 161(32), 159(35), 155(48), 149(34), 147(44), 137(100), 123(66), 121(80), 119(61), 109(98), 107(XX), 105(XX), 97(66), 95(XX), 93(XX), 91(XX), 89(39), 83(XX), 81(XX), 65(49), 57(XX), 55(XX), 53(49), 51(27), 50(8).

$(2M+H)^+ 805$.

$(M+Na)^+ 425(99), 403(7), 385(20), 367 (12), 349(10), 323(9), 271(6), 199(67), 176(27), 175(87), 173(98), 161(16), 159(17), 121(44), 119(35), 111(17),$
1.57

107(80), 105(74), 97(32), 95(XX),
93(100), 91(XX), 83(65), 81(XX),
79(XX), 77(88), 71(81), 65(35), 61(53),
57(XX), 55(XX), 53(64), 51(24), 50(8).
REFERENCES


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