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# X-Ray Crystallographic Studies of 6-Oxa-B-homo-5 $\alpha$ -cholestan-7-one, A Modified Steroids

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**ABSTRACT:** The first complete X-ray crystal structure analysis of a steroid (cholesteryl iodide) including determination of atomic coordinates was done<sup>9</sup>. Since that time full crystal structure determination have been published for few steroids. These were class of estranes, androstanes, pregnanes, cholanes, cholestanes, steroid alkaloids, ergostanes, lanostanes, cardanolides and bufanolides. These structure determination provide a wealth of raw material concerning molecular conformation and intermolecular interactions. Current work cover the synthesizing, characterization and complete x-ray crystallography study of 6-oxa-B-homo 5 $\alpha$ -cholestance-7-one (XV). The assigned structure elucidated with the help of IR, 1H-NMR, Mass and further supported by X-Ray crystallography. The result obtained were molecular formula C<sub>27</sub>H<sub>46</sub>O<sub>2</sub>, molecular weight 402.66, crystal morphology, colorless plate, Lattice parameters a=5.971(2), b=11.043(1), c=19.243(1) Å, space group, P2<sub>1</sub>, Z=2 (two molecule per unit cell), Density (D<sub>c</sub>) 1.062, radiation,  $wk\alpha(\lambda=1.54178\text{Å})$ , temperature 23°C. The most important data obtained by X-ray crystallography are bond length, bond angle and different structural and conformational shape of the molecule.

**KEYWORDS:** Characterization, doublets, Multiplets centered at, X-ray crystallography, Triplet

## I. INTRODUCTION

In recent years X-ray methods have been increasingly used for quantitative and quantitative analysis as well as for fundamental studies of the properties and structures of various classes of compounds, both organic and inorganic compounds. X-ray diffraction is the only convenient and hence widely used physical procedure for the complete determination of molecular structure.

X-rays were discovered by W. C. Rontgen in 1895 in the course of a systematic study to see if any radiation could be produced which would traverse matter opaque to ordinary light. He observed that when cathode rays produced in a highly evacuated discharge tube, strike a metal target (called an anticathode), new radiations were produced which he called X-ray for their nature were not known. The X-rays were found to be more penetrating than cathode rays. They affect a photographic plate, excite fluorescence in some compound and produce ionization in gases. The radiations behave in non corpuscular manner. They are not deflected by electrical or magnetic fields. They therefore do not consist of charged particles, they are electromagnetic waves analogous to light waves but of much shorter wave length. X-rays are diffusely scattered by all substances and are partially absorbed by matter of all kinds. The most useful method by which X-rays can be used is X-ray diffraction method which involves the diffraction of X-rays from the plane of the crystals. The property of X-ray gives a analytical technique-X-ray crystallography which is now most useful method for structure elucidation of organic compounds with special reference to conformational analysis.

Richard W. Schevitz [Schevitz 1969] and co-workers reported the structure of (+) -cis carvone tribromide (1) by matter of all kinds. The most useful method by which X-rays can be done. The structure of ophiobolin, a C<sub>25</sub> terpenoid having a novel skeleton was studied by S. Tamura et al [Nozoe 1965]. X-ray crystallographic analysis, of D-(+)-2-benzyl glutamic acid was done by Tamaichi Ashida and co-workers [Ashida, 1969]. The X-ray crystal structure analysis of N-(Isopropylamino)-3,4-endo-(9', 10'-dihydroanthracene 9', 10'-diyl)-5-exohydroxy-2-pyrrolidone was done by S. M. Verma and co-workers [Srivastava 1994]. Rajnikant and co-worker studied the crystal structure of 3P-acetoxy-20-oximino-pregnane (V) [Singh, 1994]. During the studies of Fridel Crafts acylation followed by hydrolysis of hydrindane J.W. Rasbun and co-workers [Davison 1993]. Rajnikant and co-workers<sup>^</sup> reported the results of X-ray analysis of 3 $\beta$ ,20-diacetoxy-16 $\alpha$ -methyl-allopregn-17 (20)-ene [Singh 1994]. Vivek K. Gupta and coworkers studied the crystal structure of 20 $\alpha$ -propyl amino-3 $\beta$ -hydroxy-pregn-5-ene [Gupta 1994].

## II. MATERIALS, METHODS AND CHARACTERIZATION

### II.a Materials and characterization

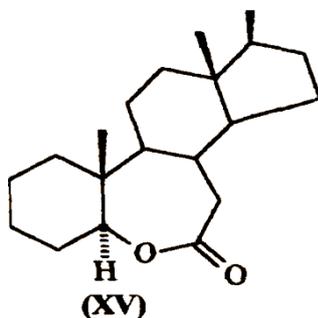
All melting points were observed on a Kofler hot block apparatus and are uncorrected. IR spectra were obtained in KBr unless otherwise specified and the IR values given are in  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  spectra were run in  $\text{CDCl}_3$  with  $\text{Me}_4\text{Si}$  as the internal reference and values are given in ppm ( $\delta$ ) (s, singlet; br, broad; d, doublet; dd, double doublet; triplet; mc, multiples 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 °C. Silica gel (-20) was used for each gram of the material to be separated in column chromatography. All glass wares were heated fraction of b.p. 40 - 60 °C. Silica gel (-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. Programs for crystal structure determination Shelves [Duax, 1976].

Baeyer Villiger oxidation of 5 $\alpha$ -cholestan-6-one gave 6-oxa-B-homo-5 $\alpha$ -cholestan-7-one (XV). 5 $\alpha$ -Cholestan-6-one (2.0 g) was treated with chloroform solution of perbenzoic acid (2.5 ml equivalent) and few crystals of p-toluene-sulphonic acid for 96 hrs. The progress of reaction was monitored by TLC. After the completion of reaction, the reaction mixture was poured into ice water and extracted with ether. The ethereal layer was washed with water, sodium bicarbonate solution (5%) and finally with water and dried over anhydrous sodium sulphate. Removal of the solvents gave a semi solid material (1.85 g) which was chromatographed over silica gel (~ 40 g).

### II.b Characterization of 6-Oxa-B-homo-5 $\alpha$ -cholestan-7-one (XV) :

Elution : Pet. ether : ether (10 : 1). Solvent of crystallization : Petroleum ether, Yield : (0.85 g), m.p. 147-148° (reported, m.p. 148°). Analysis found : C, 80.30; H, 11.14, required were C, 80.06; H, 11.44%, CD :  $[\alpha]_D^{25} = +28^\circ$  IR :  $\nu_{\text{max}}$  1735 (C=O), 1270  $\text{cm}^{-1}$  (C-O).  $^1\text{H-NMR}$ : 6.19 (dd, 1H, H-5a,  $J_{\text{aa}} = 15 \text{ Hz}$ ,  $J_{\text{ae}} = 5.5 \text{ Hz}$ ), 2.50 (brs, 1H, C7aP-H), 2.45 (d, 1H, C7aa-H,  $J = 3.5 \text{ Hz}$ ) 1.1 (ClO-CH<sub>3</sub>), 0.67 (Cl3-CH<sub>3</sub>), 0.95 and 0.85 (side chain methyl protons).  $^{13}\text{C-NMR}$  : C1(29.421), C2(25.317), C3(22.206), C4(39.441), C5-O-(83.860), -C6-O-(175.152), C7(39.783), C8(34.92), C9(55.622), C10(40.124), C11(21.372), C12(38.228), C13(42.681), C14(58.732), C15(23.761), C16(27.979), C17(56.441), C18(11.799), C19(18.550), C20(35.679), C21(12.276), C22(35.952), C23(24.535), C24(38.364), C25(27.979), C26(22.525) and C27(22.783).

Mass : m/z 402 (M<sup>+</sup>, 18.5), 387 (M<sup>+</sup> -CH<sub>3</sub>, 7), 384 (M<sup>+</sup> -H<sub>2</sub>O, 17.5), 374 (M<sup>+</sup> -CO, 12.5), 360 (M<sup>+</sup> -CH<sub>2</sub>=C=O, 6), 359 (m/z 374 -CH<sub>3</sub>, 13), 356 (m/z 384 -CO, 9), 318 (m/z 374 -C<sub>4</sub>H<sub>8</sub>, 100), 317 (m/z 318 -H; 21), 303 (16), 289 (5), 262 (7.5), 247 (8.5), 219 (6) and 178 (16)



Structure of 6-Oxa-B-homo-5 $\alpha$ -cholestan-7-one (XV)

### III. RESULTS AND DISCUSSION

#### III. a Results and discussions :

During the preparation of oxasteroids, when 5 $\alpha$ -cholestan-6-one (XXII) was treated with perbenzoic acid in chloroform (p-toluene sulphonic acid as 17 catalyst), 6-oxa-B-homo-5 $\alpha$ -cholestan-7-one (XV) (Fig. 1) was obtained which was characterized by (IR, <sup>1</sup>H-NMR, Mass)[Feroz 1998]. The assigned structure was further supported by X-ray crystallography. The results obtained were : molecular supported by X-ray crystallography[Shafiullah 1991].

The results obtained were : molecular formula; C<sub>27</sub>H<sub>46</sub>O<sub>2</sub>, molecular weight; 402.66, crystal morphology; colorless plate, crystal dimension (mm); 0.10 x 0.20 x 0.10, crystal system; monoclinic. Lattice parameters; a = 5.971 (2), b = 11.043(1), c = 19.243(1) Å, space group; P2<sub>1</sub>, Z = 2 (two molecules per unit cell). Density (D<sub>c</sub>); 1.062 g/cm<sup>3</sup>, radiation; wka (X = 1.54178Å<sup>0</sup>), temperature; 23 °C, structure solution; Patterson method.

The most important data obtained by X-ray crystallography are bond length and bond angle and different structural and conformational shape of the molecule. These structure determinations provided a wealth of raw material concerning molecular conformation and intermolecular interactions.

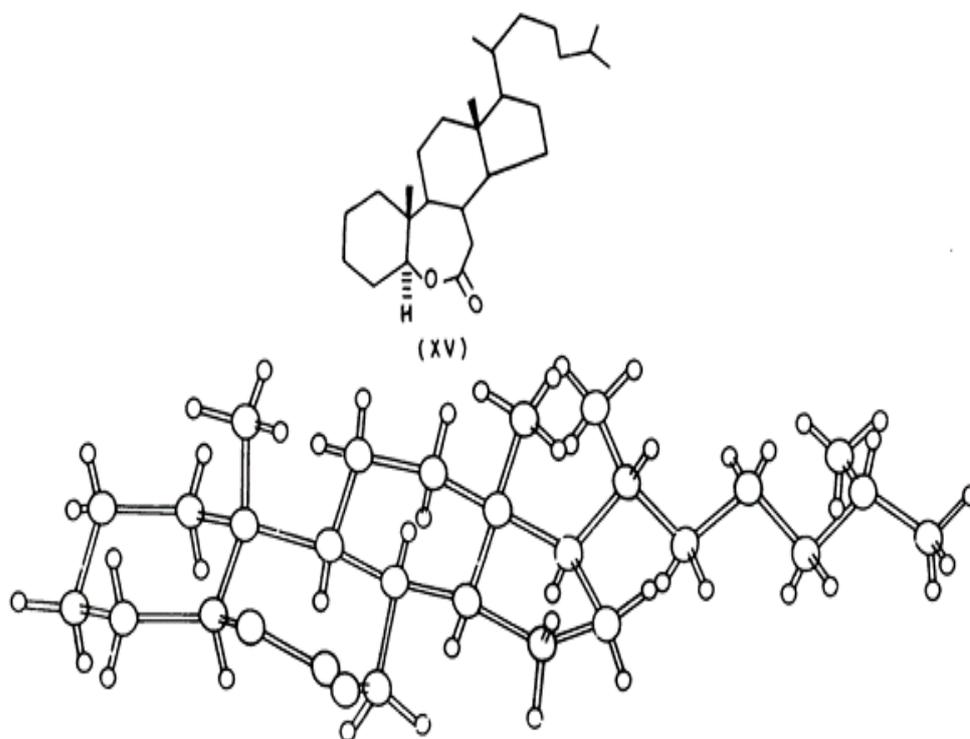


Fig.1 : General view of moiety of 6-Oxa-B-homo-5 $\alpha$ -cholestan-7-one (XV)



Table 1.0 shows intramolecular hydrogen bond of 6-oxa-B-Homo-5 $\alpha$ -cholestane-7-one (XV)

**Table - 1**

**Intramolecular distances involving hydrogen atoms**

Atom	Atom	Distance	Atom	Atom	Distance
O1	C6	1.21 (1)	C14	H18	0.970
O2	C5	1.47 (1)	C15	C16	1.54 (2)
O2	C6	1.36 (1)	C15	H19	0.911
C1	C2	1.51 (2)	C15	H20	0.999
C1	C10	1.56 (2)	C16	C17	1.56 (2)
C1	H1	0.980	C16	H21	0.970
C1	H2	0.913	C16	H22	0.969
C2	C3	1.54 (2)	C17	C20	1.53 (2)
C2	H3	0.910	C17	H23	0.964
C2	H4	0.954	C18	H24	0.950
C3	C4	1.53 (2)	C18	H25	0.950
C3	H5	0.953	C18	H26	0.921
C3	H6	0.943	C19	H27	0.966
C4	C5	1.51 (2)	C19	H28	0.912
C4	H7	0.936	C19	H29	0.924
C4	H8	0.905	C20	C21	1.52 (2)



C5	C10	1.53 (2)	C20	C22	1.54 (2)
C5	H9	0.973	C20	H30	0.964
C6	C7	1.51 (1)	C21	H31	0.964
C7	C8	1.55 (2)	C21	H32	0.947
C7	H10	0.978	C21	H33	0.956
C7	H11	0.954	C22	C23	1.50 (2)
C8	C9	1.53 (1)	C22	H34	0.928
C8	C14	1.53 (1)	C22	H35	0.997
C8	H12	0.980	C23	C24	1.52 (2)
C9	C10	1.59 (2)	C23	H36	0.938
C9	C11	1.56 (2)	C23	H37	0.917
C9	H13	0.973	C24	C25	1.51 (2)
C10	C19	1.55 (2)	C24	H38	0.873
C11	H14	0.943	C24	H39	0.995
C11	H15	0.940	C25	C26	1.48 (3)
C12	C11	1.51 (2)	C25	C27	1.39 (3)
C12	H16	0.935	C25	H40	0.925
C12	H17	0.944	C26	H41	0.878
C13	C12	1.54 (2)	C26	H42	1.009
C13	C17	1.54(2)	C26	H40	0.954
C13	C18	1.56(2)	C27	H44	0.939
C14	C13	1.50(2)	C27	H45	0.993
C14	C15	1.53(2)	C27	H46	1.015

Distances are in angstrom. Estimated standard deviations in the least significant are given in parenthesis.

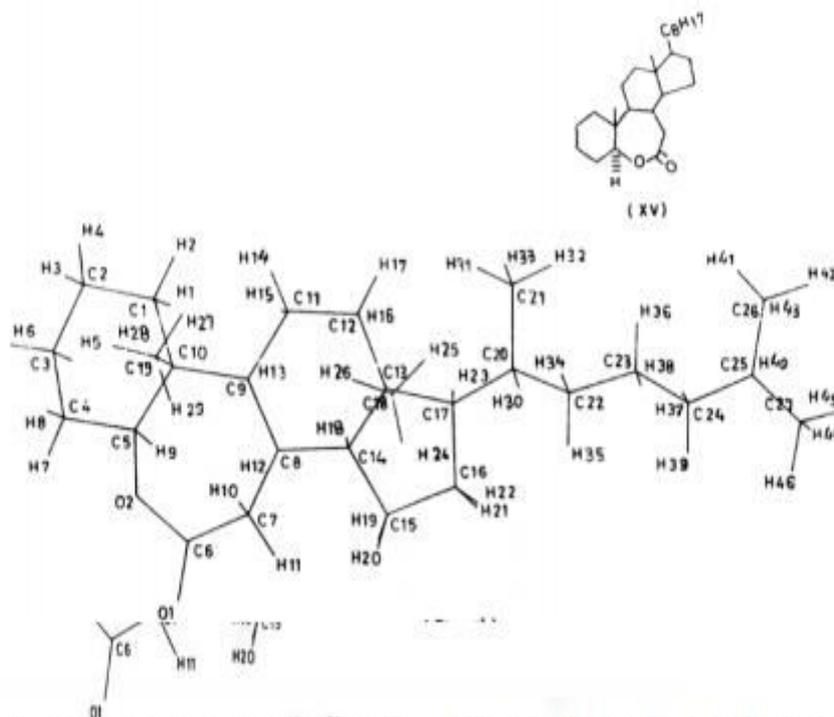


Figure 2.0 showing atomic arrangement and numbering of 6-oxa-B-homo-5α-cholestane-7-one (XV)

Table 2.0 shows intramolecular bond angle involving the hydrogen atom of 6-oxa-B-Homo-5α-cholestane-7-one (XV)

**Table - 2**

**Intramolecular bond angles involving the hydrogen atoms**

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C5	O2	C6	122 (1)	C8	C14	C18	104.16
C2	C1	C10	116 (1)	C13	C14	H15	104 (1)
C2	C1	H1	108.44	C13	C14	H18	108.53
C2	C1	H2	109.50	C14	C15	C16	104 (1)
C10	C1	H1	105.95	C14	C15	H19	112.44
C10	C1	H2	107.25	C14	C15	H20	108.78
H1	C1	H2	109.97	C16	C15	H19	114.24
C1	C2	C3	110 (1)	C16	C15	H20	108.94



C1	C2	H3	110.45	H19	C15	H20	108.51
C1	C2	H4	108.42	C15	C16	H22	108.60
C3	C2	H3	109.14	C17	C16	H21	122.16
C3	C2	H4	106.09	C17	C16	H22	111.25
H3	C2	H4	112.70	H21	C16	H22	106.28
C2	C3	C4	108 (1)	C13	C17	C16	103 (1)
C2	C3	H5	111.53	C13	C17	C20	121 (1)
C2	C3	H6	110.34	C13	C17	H23	109.92
C4	C3	H5	109.71	C16	C17	C20	111 (1)
C4	C3	H6	106.94	C16	C17	H23	105.59
H5	C3	H6	109.83	C20	C17	H23	104.97
C3	C4	C5	111 (1)	C13	C18	H24	106.63
C3	C4	H7	107.19	C13	C18	H25	105.91
C3	C4	H8	108.40	C13	C18	H26	106.52
C5	C4	H7	108.40	H24	C18	H25	111.29
C5	C4	H8	106.87	H24	C18	H26	112.01
H7	C4	H8	114.82	H25	C18	H26	113.89
O2	C5	C4	103 (1)	C10	C19	H28	107.80
O2	C5	C10	113 (1)	C10	C19	H29	107.34
O2	C5	H9	102.54	H27	C19	H28	111.39
C4	C5	C10	116 (1)	H27	C19	H29	110.36
C4	C5	H19	108.57	H28	C19	H29	115.35
C4	C5	H9	112.93	C21	C20	H30	107.71
O1	C6	O2	114 (1)	C22	C20	H30	107.70
O1	C6	C7	127 (1)	C17	C20	C21	115 (1)
O2	C6	C7	119 (1)	C17	C20	C22	110 (1)
C6	C7	C8	110 (1)	C17	C20	H30	107.23



C6	C7	H10	109.38	C21	C20	C22	110 (1)
C6	C7	H11	104.28	C20	C21	H31	109.89
C8	C7	H10	111.37	C20	C21	H32	111.39
C8	C7	H11	114.80	C20	C21	H33	109.91
H10	C7	H11	106.85	H31	C21	H32	103.55
C7	C8	C9	113 (1)	H31	C21	H33	107.80
C7	C8	C14	106 (1)	H32	C21	H33	109.22
C7	C8	H12	108.19	C20	C22	C23	116 (1)
C9	C8	C14	108 (1)	C20	C22	H34	108.8
C9	C8	H12	110.70	C20	C22	H35	105.85
C14	C8	H12	109.95	C23	C22	H34	111.29
C8	C9	C10	119 (1)	C23	C22	H35	106.56
C8	C9	H14	111 (6)	H34	C22	H35	107.28
C8	C9	H13	103.18	C22	C23	C24	113 (2)
C10	C9	C11	110 (1)	C22	C23	H36	104.49
C10	C9	H13	105.07	C22	C23	H38	108.40
C11	C9	H13	107.81	C24	C23	H36	105.43
C1	C10	C5	107 (1)	C24	C23	H37	111.46
C1	C10	C9	107 (1)	H36	C23	H37	113.57
C1	C10	C19	110 (1)	C23	C24	C25	110 (2)
C5	C10	C9	110 (1)	C23	C24	H37	113.77
C5	C10	C19	111 (1)	C23	C24	H39	105.29



C8	C9	C10	119 (1)	C23	C22	H35	106.56
C8	C9	H14	111 (6)	H34	C22	H35	107.28
C8	C9	H13	103.18	C22	C23	C24	113 (2)
C10	C9	C11	110 (1)	C22	C23	H36	104.49
C10	C9	H13	105.07	C22	C23	H38	108.40
C11	C9	H13	107.81	C24	C23	H36	105.43
C1	C10	C5	107 (1)	C24	C23	H37	111.46
C1	C10	C9	107 (1)	H36	C23	H37	113.57
C1	C10	C19	110 (1)	C23	C24	C25	110 (2)
C5	C10	C9	110 (1)	C23	C24	H37	113.77
C5	C10	C19	111 (1)	C23	C24	H39	105.29
C9	C10	C19	111 (1)	C25	C24	H37	110.96
C9	C11	C12	115 (1)	C25	C24	H39	104.55
C9	C11	H14	106.15	H37	C24	H39	112.07
C9	C11	H15	105.70	C24	C25	C26	112 (2)
C12	C11	H14	109.10	C24	C25	C27	113 (2)
C12	C11	H15	110.05	C24	C25	H40	109.40
H14	C11	H15	110.96	C26	C25	H40	106.68
C13	C12	C11	110 (1)	C27	C25	H40	103.31

#### IV. CONCLUSION

Due to ring enlargement from sixmembered to seven membered and lactone moiety having sp<sup>2</sup> hybridized carbon lactone (XV) with tendency to have planar geometry suffers deformation in seven membered B -ring. It is pertinent to mention that ring C also suffers slight conformational change.

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