

( $254 \times 10^{-6}/^{\circ}\text{C}$ ) being much greater than in the **a** and **b** directions ( $33 \times 10^{-6}$  and  $28 \times 10^{-6}/^{\circ}\text{C}$ , respectively). Thus, the length of the **c** axis is reduced by 3.0% when the temperature is decreased from room temperature to  $-160^{\circ}\text{C}$  whereas the lengths of the **a** and **b** axes are reduced by only 0.4 and 0.3% respectively, during the same temperature span. On the other hand, the C(5)···N(2) separation remains essentially the same ( $3.30 \text{ \AA}$ ) at both temperatures. Fig. 6 illustrates the packing of the sheets viewed down the **b** axis.

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## Oxido Steroids I: The Crystal Structure of 11 $\beta$ , 12 $\alpha$ -Dibromo-3 $\alpha$ , 9-oxidocholanic Acid Methyl Ester

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The crystal structure of 11 $\beta$ , 12 $\alpha$ -dibromo-3 $\alpha$ , 9-oxidocholanic acid methyl ester,  $\text{C}_{25}\text{H}_{38}\text{O}_3\text{Br}_2$ , has been determined using three-dimensional X-ray diffraction data. This steroid crystallizes from acetone solution in the orthorhombic space group  $P2_12_12_1$  with four molecules per unit cell with dimensions:  $a = 14.472 \pm 0.003$ ,  $b = 20.587 \pm 0.005$ , and  $c = 7.990 \pm 0.001 \text{ \AA}$ . The *A* ring is boat shaped, and rings *B* and *C* are chair shaped. The mean plane through the atoms of the *A* ring is practically perpendicular ( $92^\circ$ ) to the mean plane of the *B* ring and the mean planes of rings *B*, *C*, and *D* are all nearly parallel to each other. The atoms forming the side chain attached to C(17), with the exception of C(21), lie approximately in a plane which is inclined to the mean plane of the *D* ring at an angle of  $104^\circ$ . Molecules are held together in the crystalline state by van der Waals forces.

#### Introduction

Investigation of the crystal structure of a variety of steroids, steroid derivatives, and steroid complexes

constitutes an integral part of the program underway in our laboratory to correlate the biological activity of steroids with their molecular structures. In as much as oxido steroids are known to be convenient intermediates for passing from mono-substituted to di-substituted compounds or *vice versa*, and that combination of these two processes can in some cases provide a means of transferring a substituent from one carbon atom to another, it is reasonable to expect that certain biologi-

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cal roles of steroids may be mediated by oxido bonds.

The bile acid, 3 $\alpha$ ,9-oxido- $\Delta^{11}$ -cholanic acid methyl ester, may be brominated by careful addition of bromine to dry chloroform solution accompanied by cooling in a dry ice/acetone bath as described by Mattox, Turner, Engel, McKenzie, McGuckin & Kendall (1946 *a, b*, 1948). The yield consists of two isomers, an 11 $\beta$ ,12 $\alpha$ -dibromo derivative (65%), and an 11 $\beta$ ,12 $\beta$ -dibromo derivative (35%). Mattox *et al.*, in their papers, mention the latter isomer as the 11 $\alpha$ ,12 $\beta$ -dibromo derivative; however, our X-ray structure investigation (Gopalakrishna, Cooper & Norton, 1968) has established it as the 11 $\beta$ ,12 $\beta$ -dibromo derivative. When the  $\beta$ , $\alpha$  derivative is shaken with silver oxide or silver carbonate in aqueous acetone, the 11 $\beta$ -bromine atom is replaced by a hydroxyl group producing 12 $\alpha$ -bromo-11 $\beta$ -hydroxy-3 $\alpha$ , 9-epoxycholanic acid methyl ester. The  $\beta$ , $\beta$  derivative, on the other hand, resists similar attempts to eliminate one of the bromine atoms. The structure of the  $\beta$ , $\alpha$  derivative is reported in this paper. Fig. 1 shows a schematic representation of the molecule with the atoms numbered for reference in the text.

### Experimental

Transparent, colorless, acicular crystals, elongated along the *c* axis, were grown by slow evaporation of a solution of 11 $\beta$ , 12 $\alpha$ -dibromo-3 $\alpha$ , 9-oxidocholanic acid methyl ester in acetone. The specimen used for X-ray analysis was 0.165 mm in length and was cut from a longer crystal of cross-section 0.09  $\times$  0.3 mm. All X-ray measurements were made on a General Electric single crystal counter diffractometer unit using Cu  $K\alpha$  radiation. The crystal was mounted with its *c* axis parallel to the  $\phi$  axis of the instrument.

The systematic extinctions ( $h00$  for  $h=2n+1$ ,  $0k0$  for  $k=2n+1$ ,  $00l$  for  $l=2n+1$ ) placed the crystal in the orthorhombic space group  $P2_12_12_1$ . The unit-cell dimensions obtained are:  $a=14.472 \pm 0.003$ ,  $b=20.587 \pm 0.005$ , and  $c=7.990 \pm 0.001$  Å measured at 20°C, Cu  $K\alpha_1=1.54051$  Å). The density of the crystal calculated on the basis of four molecules per unit cell is 1.52 g.cm<sup>-3</sup> as compared with the measured value of 1.49 g.cm<sup>-3</sup> determined by the flotation method.

Intensities were collected for 2040 independent reflections within the  $2\theta$  range 0°–160° by the stationary-crystal stationary-counter method using balanced nickel and cobalt filters, and these intensities were corrected appropriately for Lorentz and polarization factors. The intensities of the reflections for the two planes (004) with  $2\theta=45.46^\circ$  and (002) with  $2\theta=22.26^\circ$  were studied for variation with  $\phi$ -orientation due to absorption. The intensity of the (004) reflection varied up to a maximum of  $\pm 15\%$  from the mean value, and that of (002) varied up to a maximum of  $\pm 9\%$ . The crystal showed a gradual decay in intensities of about 15% over the period of ten days during which the

intensities were collected. The intensities were not corrected for absorption or for decay of the crystal. The observed structure amplitudes were placed on an absolute scale by Wilson's (1942) method and the scale factor so obtained was subsequently reduced by 7% during the least-squares refinement of the structure.

### Structure analysis

The positions of the two bromine atoms in the asymmetric unit were obtained from the three-dimensional sharpened Patterson synthesis computed with the squares of the unitary structure factors.

Calculation of structure factors with the contributions from the bromine atoms alone gave an *R* value of 45% and the remainder of the atoms in the asymmetric unit were located by straightforward application of the heavy atom method. The structure so obtained was refined by least-squares using 4  $\times$  4 matrix blocks for the positional and isotropic thermal parameters of the carbon and oxygen atoms and 9  $\times$  9 matrix blocks for the positional and anisotropic thermal parameters of the bromine atoms. The scattering factor values given in *International Tables for X-ray Crystallography* (1962) were used throughout. The weights used in the refinement were  $1/\sigma^2(|F_o|)$  where  $\sigma(|F_o|)$  is the standard deviation in the observed structure amplitude (obtained from counting statistics alone). The quantity minimized was  $\sum w(|F_o| - |F_c|)^2$ .

When the refinement of the structure was terminated the *R* value was 10.5% for the 1250 reflections whose intensities were greater than twice their respective estimated standard deviations, and 14.5% for all the 2040 reflections whose intensities were measured.

Up to this stage,  $\Delta f''_{Br}$ , the imaginary part of the anomalous dispersion factor for the bromine atom, was ignored and the scattering factors were corrected only for  $\Delta f'_{Br}$ , the real part of the anomalous dispersion factor. To decide upon the absolute configuration of the molecule, two sets of structure factors were calculated, one with  $\Delta f''_{Br} = +1.46$  and another with  $\Delta f''_{Br} = -1.46$ . Since the two solutions obtained did not

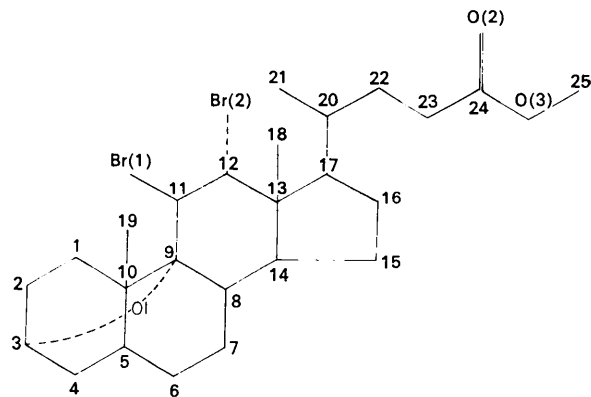


Fig. 1. Schematic representation of the molecule with the atoms numbered for reference in text.

Table 1. Observed and calculated structure amplitudes Given on ten times absolute scale

Table with multiple columns of numerical data representing structure amplitudes. The columns are organized into groups, each with a header row (e.g., H, K, L, F, OBS, CAL) and a corresponding row of values. The data is presented in a grid-like format across the page.

Table 1 (cont.)

H	K	L	F0BS	FCAL	H	K	L	F0BS	FCAL	H	K	L	F0BS	FCAL	H	K	L	F0BS	FCAL	H	K	L	F0BS	FCAL	H	K	L	F0BS	FCAL	H	K	L	F0BS	FCAL	H	K	L	F0BS	FCAL								
9 5 7	176	123	9 13	4	104	97	10	3	4	115	497	10	11	2	108	87	11	3	1	418	411	11	11	1	108	47	12	4	0	259	338	12	14	1	72	56	13	9	0	238	234	14	7	2	179	186	
9 6 0	238	247	9 13	5	176	43	10	3	4	209	239	10	11	3	108	55	11	3	1	464	546	11	11	3	238	107	12	4	0	359	338	12	14	1	72	56	13	9	0	238	234	14	7	2	179	186	
9 6 1	624	777	9 14	0	185	141	10	3	5	238	250	10	11	4	333	315	11	3	3	120	74	11	11	3	212	176	12	4	2	212	244	12	15	0	101	80	13	9	2	238	182	14	8	0	104	146	
9 6 2	212	232	9 14	1	281	210	10	3	6	147	140	10	11	5	72	141	11	3	3	120	74	11	11	3	238	107	12	4	3	238	282	12	15	0	101	14	13	9	2	206	114	14	8	0	104	146	
9 6 3	281	283	9 14	2	215	241	10	4	0	483	542	10	12	0	108	35	11	3	4	150	135	11	11	5	72	97	12	4	4	481	275	13	0	1	258	156	13	0	4	172	187	14	8	2	101	172	
9 6 4	179	207	9 14	3	150	57	10	4	1	340	346	10	12	1	353	359	11	3	5	150	196	11	12	0	320	319	12	4	5	72	119	13	0	1	258	148	13	10	0	74	18	14	8	3	144	170	
9 6 5	523	540	9 14	4	104	119	10	4	2	307	182	10	12	2	304	244	11	3	6	150	135	11	12	1	238	251	12	4	6	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 6 6	235	100	9 14	5	72	48	10	4	3	349	340	10	12	3	150	112	11	4	0	343	334	11	12	2	150	75	12	4	5	209	125	13	0	4	104	31	13	10	2	147	120	14	9	1	228	240	
9 6 7	150	150	9 15	0	215	205	10	4	4	238	31	10	13	0	147	178	11	4	1	245	243	11	13	3	238	107	12	4	6	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 6 8	483	683	9 15	1	108	110	10	4	5	74	42	10	12	5	202	140	11	4	2	144	218	11	12	4	150	135	12	4	7	215	313	13	0	1	212	253	13	11	0	74	27	14	10	0	289	236	
9 6 9	530	521	9 15	2	238	259	10	4	6	104	26	10	13	0	147	184	11	4	3	150	135	11	13	5	108	78	12	4	8	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 7 2	320	325	9 15	3	104	97	10	5	0	434	380	10	13	1	241	330	11	4	4	150	91	11	13	0	108	78	12	4	9	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 7 3	543	544	9 15	4	72	141	10	5	1	334	188	10	13	2	185	162	11	4	5	299	310	11	13	1	238	107	12	4	10	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 7 4	297	281	9 16	0	104	52	10	5	2	219	239	10	13	3	238	263	11	4	6	187	211	11	13	2	238	107	12	4	11	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 7 5	74	64	9 16	1	258	225	10	5	3	231	211	10	13	4	204	175	11	4	7	244	244	11	13	3	238	107	12	4	12	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 7 6	287	241	9 16	2	104	61	10	5	4	104	184	10	14	0	74	108	11	4	8	202	202	11	13	4	238	107	12	4	13	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 7 7	54	60	9 16	3	179	127	10	5	5	241	302	10	14	1	150	71	11	4	9	291	225	11	13	5	238	107	12	4	14	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 7 8	163	174	9 16	4	72	102	10	5	6	104	88	10	14	2	300	339	11	4	10	150	152	11	13	6	238	107	12	4	15	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 7 9	88	38	9 16	5	104	91	10	5	7	48	3	10	14	3	147	86	11	4	11	185	141	11	13	7	238	107	12	4	16	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 7 0	811	845	9 17	0	313	317	10	6	0	48	3	10	14	4	278	184	11	5	0	104	36	11	13	8	238	107	12	4	17	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 8 3	72	113	9 17	1	104	91	10	6	1	136	131	10	14	5	278	184	11	5	1	104	36	11	13	9	238	107	12	4	18	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 8 4	317	247	9 17	2	104	107	10	6	2	222	219	10	15	0	235	115	11	5	2	104	110	11	13	10	238	107	12	4	19	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 8 5	74	44	9 17	3	144	122	10	6	3	232	224	10	15	1	104	124	11	6	0	72	94	11	13	11	238	107	12	4	20	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 8 6	255	162	9 18	0	101	92	10	6	4	212	262	10	15	2	147	95	11	6	1	270	263	11	13	12	238	107	12	4	21	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 8 7	425	400	9 18	1	174	157	10	6	5	185	111	10	15	3	314	192	11	6	2	74	165	11	13	13	238	107	12	4	22	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 9 1	68	113	9 18	2	202	191	10	6	6	104	149	10	15	4	101	84	11	6	3	108	92	11	13	14	238	107	12	4	23	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 9 2	122	85	9 19	0	101	44	10	7	0	170	140	10	16	0	104	97	11	6	4	150	162	11	13	15	238	107	12	4	24	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 9 3	102	405	9 19	1	209	164	10	7	1	170	144	10	16	1	232	230	11	6	5	120	88	11	13	16	238	107	12	4	25	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 9 4	326	332	10 0	0	127	71	10	7	2	176	250	10	16	2	72	35	11	6	6	72	114	12	13	17	238	107	12	4	26	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 9 5	183	132	10 0	1	748	792	10	7	3	232	197	10	16	3	101	104	11	7	0	101	75	12	13	18	238	107	12	4	27	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 9 6	101	45	10 0	2	0	95	177	10	7	4	150	141	10	17	0	101	74	11	7	1	179	135	12	13	19	238	107	12	4	28	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104
9 10 0	194	164	10 0	3	372	432	10	7	5	183	180	10	17	1	101	59	11	7	2	333	246	12	13	20	238	107	12	4	29	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 10 1	317	323	10 0	4	104	57	10	7	6	251	170	10	17	2	202	121	11	7	3	108	140	12	13	21	238	107	12	4	30	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 10 2	176	154	10 0	5	261	245	10	8	0	72	26	10	18	0	101	69	11	7	4	108	131	12	13	22	238	107	12	4	31	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104	
9 10 3	150	169	10 0	6	74	48	10	8	1	132	10	18	1	104	75	10	7	5	120	10	12	13	23	238	107	12	4	32	411	419	13	0	5	72	91	13	10	3	204	180	14	9	2	176	104		
9 10 4	90																																														

Table 1 is a listing of observed and calculated structure amplitudes, and the final atomic coordinates and temperature factors are given in Table 2.

### Description of the structure

The bond lengths and bond angles are given in Fig. 2(a) and (b), respectively. The standard deviations are in the range 0.02–0.03 Å for bond lengths and 1.5–2.0° for bond angles. Out of the twenty-six bond lengths obtained for C(sp<sup>3</sup>)–C(sp<sup>3</sup>) single bonds, eight [C(5)–C(10), C(8)–C(9), C(9)–C(10), C(9)–C(11), C(11)–C(12), C(13)–C(18), C(13)–C(17), and C(15)–C(16)] are larger than the expected value of 1.533 Å (Bonham &

Bartell, 1959) by more than twice the estimated standard deviations. The two bonds C(3)–O(1) and C(9)–O(1) with lengths 1.51 and 1.47 Å respectively, are in good agreement with the expected value of 1.47 Å (*International Tables*, 1962) for strained carbon–oxygen single bonds in epoxides. The bonds C(11)–Br(1) and C(12)–Br(2) have lengths 2.00 and 2.03 Å respectively, and are consistent with the values obtained for similar bonds (Gopalakrishna *et al.*, 1968).

Out of the fifty bond angles obtained in this steroid, eight deviate from the usually expected values by as much as three times their estimated standard deviations. The two angles Br(1)–C(11)–C(12) and Br(2)–C(12)–C(11) with values of 101° and 100° respectively, are smaller than expected. This distortion is apparently the result of the axial substitution of the two bromine atoms at C(11) and C(12). The angle O(2)–C(24)–C(23) with a value of 132° is large. The three angles C(9)–C(10)–C(5), C(4)–C(5)–C(6) and C(5)–C(6)–C(7) with values of 102, 118, and 119° respectively, deviate from tetrahedral angles and this may be result of the oxido bridge between C(3) and C(9). The deviations of the two angles O(2)–C(24)–C(23) and C(24)–O(3)–C(25) with values of 132° and 119° respectively, appear to be related to the shortening of the bond lengths about atom O(3).

All the important torsional angles calculated for this steroid are listed in Table 3, in which the sign convention used is that of Klyne & Prelog (1960). The two torsional angles in the B ring,  $\theta(10,9)$  with a value of –69° and  $\theta(7,8)$  with a value of –54°, deviate to a certain extent from the normal staggered configuration value of 60°. This distortion in the B ring is due to the transmission of the distortion in the C ring, arising from the heavy atom substitution in the two adjacent axial positions. In the C ring,  $\theta(9,10)$ ,  $\theta(11,12)$ , and  $\theta(13,12)$  with values of +37°, –29°, and +42° respectively, reveal the extent distortion of. Two of these angles are approximately halfway between staggered and eclipsed configurations. The torsional angles in the D ring are practically the same as those in the D ring of 2 $\beta$ ,3 $\alpha$ -dichloro-5 $\alpha$ -cholestane (Brutcher & Leopold, 1966), where the D ring is also a distorted half-chair. The angle  $\theta(15,16)$  is +11° and the angle  $\theta(16,17)$  is +18°, whereas in 2 $\beta$ ,3 $\alpha$ -dichloro-5 $\alpha$ -cholestane, they are +10° and +18° respectively. (In

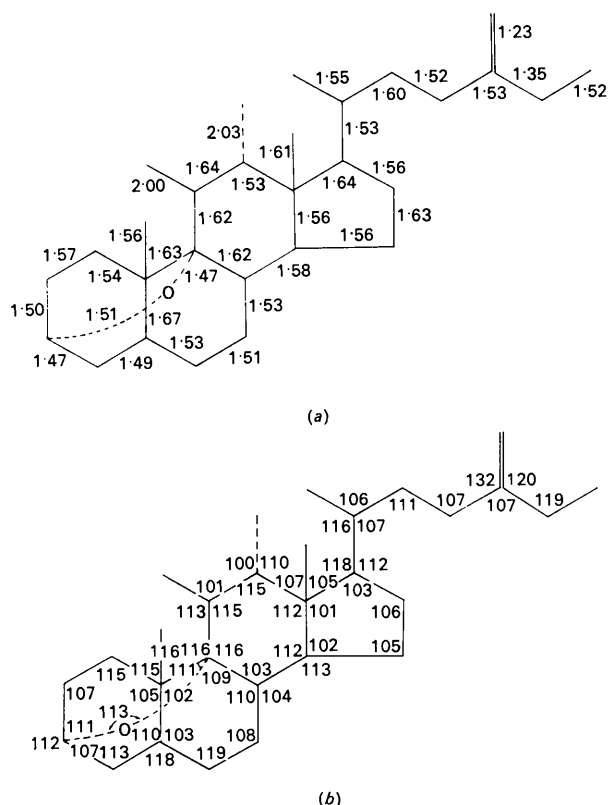


Fig. 2. (a) Interatomic distances. Standard deviations are in the range 0.02–0.03 Å. (b) Bond angles. Standard deviations are in the range 1.5–2.0°.

Table 3. Torsional angles in the rings

$\theta A-B$  is the torsional angle about the  $A-B$  bond, in which the other two atoms required to define the angle are those attached to either end of the bond and are in the ring in question.

A Ring		B Ring		C Ring		D Ring	
Bond	$\theta A-B$	Bond	$\theta A-B$	Bond	$\theta A-B$	Bond	$\theta A-B$
C(1)–C(2)	8.3	C(5)–C(6)	–64.5	C(8)–C(9)	–53.2	C(13)–C(14)	47.4
C(2)–C(3)	55.6	C(6)–C(7)	58.3	C(9)–C(11)	36.6	C(14)–C(15)	–36.6
C(3)–C(4)	–66.8	C(7)–C(8)	–53.9	C(11)–C(12)	–29.4	C(15)–C(16)	11.0
C(4)–C(5)	9.8	C(8)–C(9)	65.3	C(12)–C(13)	42.4	C(16)–C(17)	18.1
C(5)–C(10)	47.8	C(9)–C(10)	–68.9	C(13)–C(14)	–65.5	C(13)–C(17)	–40.6
C(1)–C(10)	–57.7	C(5)–C(10)	65.1	C(8)–C(14)	67.2		

a regular half-chair,  $\theta(15,16)$  will be equal to  $\theta(16,17)$  and will be approximately  $+16^\circ$  (Brutcher & Leopold, 1966).

Two perspective views of the steroid molecule are shown in Fig. 3(a) and (b) which show the main stereochemical features of the molecule. Rings *A* and *B* are *cis*-fused, and rings *B* and *C*, as well as *C* and *D*, are *trans*-fused. Ring *A*, as expected, is boat-shaped to facilitate the oxido bridging between C(3) and C(9); rings *B* and *C* are chair-shaped, and the *D* ring is a distorted half-chair. With the exception of C(21), all atoms in the side-chain attached to C(17) are coplanar to within 0.17 Å. Fig. 3(c) shows a perspective view of the side-chain as viewed in a direction parallel to this plane. The side chain is attached to C(17) in a  $\beta$ -configuration.

Equations of the least-squares planes of important portions of the molecule are given in Table 4(a) and perpendicular distances of atoms from these planes are given in Table 4(b). The *A* ring reveals very little distortion or strain. The four atoms, C(1), C(2), C(4) and C(5) lie in their mean plane,  $A_2$ , within  $\pm 0.04$  Å, and this plane is practically parallel to, and at a distance of 0.25 Å from, the mean plane of the *A* ring. Atoms C(1), C(2), C(4), and C(5) are at an average perpendicular distance of 0.23 Å from the mean plane of the *A* ring, whereas atoms C(3) and C(10) are each at a distance of 0.46 Å from this plane, and on the other side. The *A* ring, along with the oxido oxygen atom, form a regular three-ribbed cage as shown in Fig. 3(d). The *B* ring deviates slightly from an ideal cyclohexane ring: atoms C(9) and C(10) are farther away (0.36 Å) from the mean plane of the ring than the other atoms and C(7) is only 0.18 Å from that plane. As mentioned earlier, this is due to the transmission of the distortion in the *C* ring. The *C* ring is highly distorted as compared with an ideal cyclohexane ring: atoms C(11) and C(12) are only 0.08 Å from the mean plane of the *C* ring, compared with the usual distance of 0.26 Å in a strain-free cyclohexane ring. The *D* ring has a distorted half-chair conformation.

Table 4(c) gives the interplanar angles between the various least-squares planes. The mean plane of the *A* ring is almost perpendicular ( $92^\circ$ ) to the mean plane of the *B* ring. The angle between the *B* and *C* rings is  $9^\circ$  and that between the *C* and *D* rings is  $6^\circ$ . In other words, the mean planes of the *B*, *C*, and *D* rings are all nearly parallel to each other. The mean plane of the atoms in the side chain, with the exception of C(21), is inclined at an angle of  $104^\circ$  to the mean plane of the *D* ring and at  $102^\circ$  to the mean plane of the atoms C(5) through C(17). The two bonds C(10)–C(19) and C(13)–C(18) are inclined to each other at an angle of  $16^\circ$ .

#### Packing and intermolecular contacts

Fig. 4 shows the crystal structure as projected down the *c* axis of the unit cell. The molecules which are related by the screw axes parallel to *c*, are packed with their nuclei parallel to each other. All the intermolec-

ular distances are greater than the sum of the van der Waals radii of the two atoms at the intermolecular contact. There are only seventeen intermolecular contacts with distances less than 4.0 Å and only two less than 3.5 Å. The shortest contacts are between O(3) of one molecule and the *A* ring of the neighboring molecule 3.34 Å with C(2) and 3.49 Å with C(4)]. Of the remaining fifteen contacts less than 4.0 Å, six are between O(2) of one molecule and the carbon atoms of the neighboring molecules. All these intermolecular

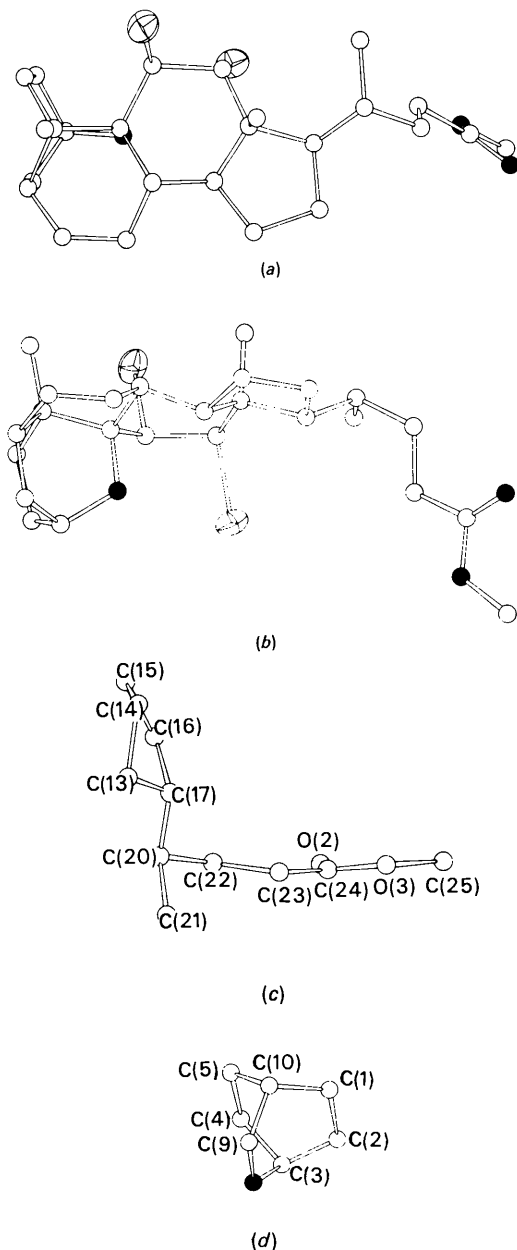


Fig. 3. Perspective view of the molecule as seen from (a) the top (b) the side. (c) Perspective view of the side chain and the *D* ring, showing the extent of planarity of the side chain. (d) Perspective view of the *A* ring and the oxido-bond, showing the 3-ribbed cage structure.

Table 4(a). Equations for the least-squares planes\*

Plane	Atoms included	<i>l</i>	<i>m</i>	<i>n</i>	<i>p</i>
A1	C(2), C(3), C(4)	0.1842	-0.9815	0.0519	5.710
A2	C(1), C(2), C(4), C(5)	-0.6705	-0.7204	-0.1774	8.397
A3B1	C(1), C(5), C(6), C(10)	-0.9474	0.0634	-0.3136	5.869
B2	C(6), C(7), C(9), C(10)	0.4275	-0.9006	0.0786	1.782
B3C1	C(7), C(8), C(9), C(11)	-0.9604	0.2376	-0.1456	3.136
C2	C(8), C(11), C(12), C(14)	0.4492	-0.8934	0.0003	1.393
C3D1	C(12), C(13), C(14), C(15)	-0.9116	0.3503	-0.2152	1.675
D2	C(13), C(15), C(16), C(17)	0.4306	-0.9021	0.0281	0.824
A4	O(1), C(9), C(1), C(2)	-0.1358	-0.3484	-0.9274	4.839
A5	O(1), C(9), C(4), C(5)	-0.5797	-0.3381	0.7413	1.439
A	C(1), C(2), C(3), C(4), C(5), C(10)	-0.6877	-0.7040	-0.1773	8.147
B	C(5), C(6), C(7), C(8), C(9), C(10)	-0.7072	0.6817	-0.1876	0.857
C	C(8), C(9), C(11), C(12), C(13), C(14)	0.6672	-0.7437	0.0425	0.162
D	C(13), C(14), C(15), C(16), C(17)	0.5942	-0.8005	0.0781	0.406
E	C(20), C(22), C(23), C(24), C(25), O(2), O(3)	-0.0508	-0.4323	-0.9003	1.282
C5-C17		0.6379	-0.7629	0.1051	0.186

\* Equations to the least-squares planes are of the form  $lX + mY + nZ + p = 0$ , where  $X$ ,  $Y$ ,  $Z$  and  $p$  are in Å units, referred to the crystallographic axes.

Table 4(b). Perpendicular distances of atoms from least-squares planes (Å)

	A1	A2	A3B1	B2	B3C1	C2	C3D1	D2	A	B	C	D	E	C(5)-C(17)
C(1)		0.04	-0.04						0.29					
C(2)	0.00	-0.04							0.18					
C(3)	0.00								-0.48					
C(4)	0.00	0.04							0.25					
C(5)		-0.04	0.04						0.20	-0.30				-0.47
C(6)			-0.04	-0.07						0.23				0.10
C(7)				0.07	-0.10					-0.18				-0.14
C(8)					0.09	0.13				0.24	0.32			0.44
C(9)				-0.06	0.11					-0.35	-0.18			-0.17
C(10)			0.04	0.07					-0.45	0.36				0.36
C(11)					-0.10	-0.13					0.08			0.02
C(12)						0.14	-0.04				-0.09			-0.11
C(13)							0.05	0.07			0.23	0.30		0.31
C(14)						-0.14	0.03				-0.36	-0.29		-0.21
C(15)							-0.04	-0.07				0.15		0.19
C(16)								0.11				0.03		-0.04
C(17)								-0.11				-0.19		-0.27
C(20)														0.13
C(22)														0.01
C(23)														-0.17
C(24)														-0.11
C(25)														0.12
O(2)														0.00
O(3)														0.02

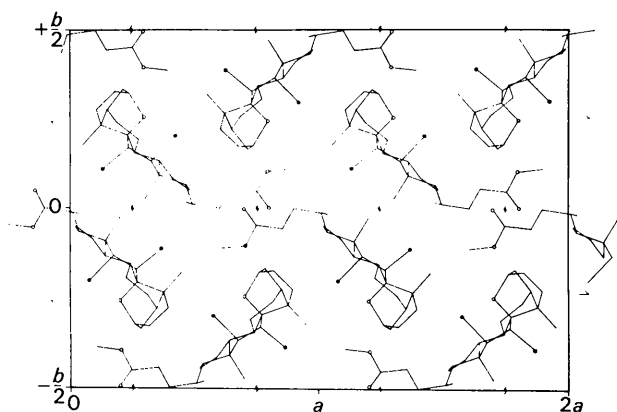


Fig. 4. Projection of two unit cells down the  $c$  axis. Open circles are oxygen atoms, closed circles are bromine atoms.

Table 4(c). Interplanar angles

Plane 1	Plane 2	Angle
A	B	92°
B	C	9
C	D	6
A	C(5)-C(17)	95
B	C(5)-C(17)	8
C	C(5)-C(17)	4
D	C(5)-C(17)	4
E	D	104
E	C(5)-C(17)	102
A1	A2	125
A2	A3B1	130
A3B1	B2	119
B2	B3C1	129
B3C1	C2	130
C2	C3D1	136
C3D1	D2	136
A2	A4	60
A4	A5	61
A5	A2	60

distances are listed in Table 5. These distances indicate that the molecules are all held together in the crystal-line state mainly by van der Waals forces.

Table 5. *Intermolecular contacts less than 4.0 Å*

Contact	Position*	Distance
C(1)—Br(2)	4/000	3.97
C(2)—C(23)	4/000	3.63
C(4)—C(23)	4/001	3.84
C(4)—C(24)	4/001	3.67
C(16)—C(25)	2/ $\bar{1}$ 00	3.81
C(16)—Br(1)	2/000	3.95
C(18)—Br(1)	2/000	3.98
C(22)—C(25)	2/ $\bar{1}$ 00	3.98
C(23)—C(2)	4/ $\bar{1}$ 00	3.63
C(23)—C(4)	4/ $\bar{1}$ 01	3.84
C(24)—C(4)	4/ $\bar{1}$ 01	3.67
C(25)—C(16)	2/ $\bar{1}$ 0 $\bar{1}$	3.81
C(25)—C(22)	2/ $\bar{1}$ 0 $\bar{1}$	3.98
O(2)—C(16)	2/ $\bar{1}$ 0 $\bar{1}$	3.80
O(2)—C(23)	2/ $\bar{1}$ 00	3.54
O(2)—C(24)	2/ $\bar{1}$ 00	3.66
O(2)—O(3)	2/ $\bar{1}$ 00	3.99
O(2)—C(2)	3/0 $\bar{1}$ 0	3.68
O(2)—C(3)	3/0 $\bar{1}$ 0	3.87
O(3)—C(2)	4/ $\bar{1}$ 00	3.34
O(3)—3C(1)	4/ $\bar{1}$ 00	3.95
O(3)—C(4)	4/ $\bar{1}$ 01	3.49

\* Equivalent position nomenclature: C(23)—C(4) 4/ $\bar{1}$ 01 is taken to mean that C(4) is at equivalent position 4, translated  $-1, 0$  and  $+1$  unit cells in the  $a, b$  and  $c$  directions, respectively. The equivalent positions are:  $1 = (x, y, z)$ ;  $2 = (\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z)$ ;  $3 = (\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z)$ ;  $4 = (\frac{1}{2} + x, \frac{1}{2} - y, \bar{z})$ .

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## The Identification and Crystal Structure of a Hydropericardium-Producing Factor: 1,2,3,7,8,9-Hexachlorodibenzo-*p*-dioxin

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A crystalline material, isolated from a contaminated animal feed fat, and capable of producing hydropericardium in chicks, was shown by solution of its crystal structure to be 1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin (C<sub>12</sub>O<sub>2</sub>H<sub>2</sub>Cl<sub>6</sub>). The triclinic unit cell has the dimensions  $a = 7.952 \pm 0.005$ ,  $b = 9.379 \pm 0.01$ ,  $c = 9.433 \pm 0.01$  Å,  $\alpha = 92.35^\circ \pm 0.20^\circ$ ,  $\beta = 92.39^\circ \pm 0.20^\circ$ ,  $\gamma = 109.92^\circ \pm 0.30^\circ$ . The calculated density is 1.958 g.cm<sup>-3</sup> for  $Z = 2$ , compared with 2.01 g.cm<sup>-3</sup> measured for the bulk material. A statistical treatment of the 1158 measured reflections indicated a center of symmetry; the space group was therefore assumed to be *P* $\bar{1}$ . The structure was solved by the symbolic addition method of Karle & Karle. The nearly planar molecules are almost parallel to the (0 $\bar{1}$ 1) crystallographic planes. No unusual bond lengths or angles were found. The structure was refined to  $R = 10.5\%$ .

### Introduction

The isolation, chemical analyses, and spectroscopic data on the hydropericardium toxic factor (HPTF) material have been described by Wootton, Artman & Alexander (1962), and by Wootton & Courchene

(1964). One of the active fractions of material isolated was that called  $\alpha$ -3.17, where this nomenclature refers to the vapor phase chromatographic behavior as described by Wootton *et al.* (1962). Wootton and his colleagues proposed that HPTF was a chlorinated hexahydrophenanthrene with the empirical formula C<sub>14</sub>H<sub>10</sub>Cl<sub>6</sub>. Following the molecular identification herein reported, Wootton (1966) showed that a synthetic hexachlorinated dibenzo-*p*-dioxin, whose physical properties are remarkably similar to the isolated

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