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Structure of 2,4,6-Tribromocholest-4-en-3-one

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Abstract. $C_{27}H_{41}Br_3O$, monoclinic, $P2_1$, a = 20·884 (4), b = 8·648 (2), c = 7·613 (2) Å, β = 92·57 (3)°, D_x = 1·502 Mg m^{-3} for Z = 2. The structure was solved by the heavy-atom method from 1728 four-circle X-ray diffractometer single-crystal data. The crystal structure was refined by the full-matrix least-squares method to a final R value of 0·083 (R_w = 0·076). The steroid rings A, B, C and D are *trans*-fused.

Introduction. The present work forms part of a stereochemical and synthetic investigation* of the dioxane dibromide (DBr_2) bromination of steroidal ketones.

Ambiguities in the interpretation of IR, UV, NMR and mass-spectral data, as well as the interpretation of ORD curves† for compounds (III) and (IV) (Fig. 1), prompted us to turn to X-ray crystallography for the positive identification of these structures. The present paper deals with the structure of the title compound (IV), whereas the crystal structure of (III) will appear later. The stereochemistry of the product (II) was assigned from its chemical correlation with compounds (III) and (IV).

Prismatic crystals of the steroid were grown by recrystallization from ethanol solution. Preliminary cell dimensions were obtained from Weissenberg and oscillation photographs using Cu $K\alpha$ (Ni-filtered) radiation. Systematic absences of $0k0$ reflexions for k odd were consistent with space group $P2_1$ (No. 4). A crystal of approximate dimensions 0·14 × 0·12 × 0·18 mm was used to collect the intensity data on a Philips PW 1100 single-crystal diffractometer using Mo $K\alpha$

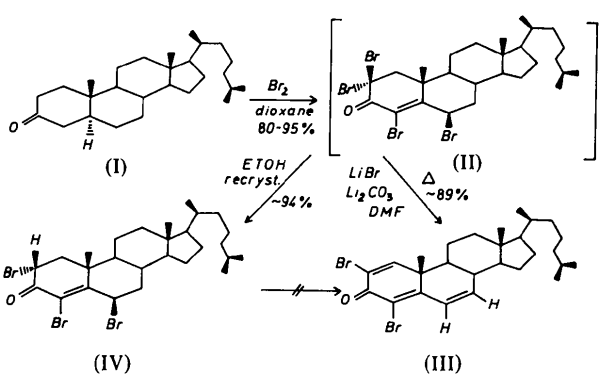

Fig. 1. The procedure for the isolation of 2,4,6-tribromocholest-4-en-3-one.

* Details of the synthesis and stereochemistry of polybrominated steroids will be published elsewhere (I. V. Mićović, to be published).

† We wish to express our appreciation to Professor Dr G. Snatzke, Ruhr-Universität Bochum, for interpretations of the ORD curves.

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radiation. The cell dimensions were calculated by the least-squares refinement of 19 reflexions having high 2θ values, and 1728 independent reflexions with $I \geq 3\sigma(I)$ were collected using ω–2θ scanning techniques. The crystal decomposed during the data collection and measurements were completed when the standard reflexion achieved 75% of its initial value. The coordinates of the Br atoms were determined from a three-dimensional Patterson synthesis. Positions of the remaining nonhydrogen atoms were found by the calculation of a few successive cycles of full-matrix least squares followed by a difference Fourier synthesis. Least-squares refinement with isotropic temperature parameters reduced R to 0·160. At this stage, the Br atoms, the O atom and the C atoms not belonging to the steroid nucleus were allowed to vibrate anisotropically and the R value dropped to 0·098.

Finally, several cycles of anisotropic refinement, followed by a difference Fourier map, were calculated, revealing more than half the H atoms. The rest were deduced from geometrical considerations. The parameters of the H atoms were fixed, with temperature factors of 4·5 Å^2. The final R value was 0·083 and R_w was 0·076, where $R = \sum||F_o| - |F_c||/\sum F_o$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, with $w = 1/\sigma^2(F)$. No absorption correction was applied ($\mu_{MoK\alpha} = 4{\cdot}55$ mm^{-1}). The scattering factors for Br, C, O and H atoms, as well as f' and f'' for the Br atom, were taken from *International Tables for X-ray Crystallography* (1974). The final atomic parameters are given in Table 1.*

All calculations were performed on a CDC-3600 computer. Programs employed include the Fourier summation program of A. Zalkin (unpublished),

Table 1. *Atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* (Å^2)

	x	y	z	B_{eq}/B
Br(1)	−708 (1)	4999 (3)	8252 (3)	6·60 (0·07)*
Br(2)	376 (1)	10770 (3)	6980 (3)	5·70 (0·06)*
Br(3)	2206 (1)	9622 (–)	8039 (3)	6·77 (0·07)*
O	−525 (6)	8427 (18)	8183 (23)	9·24 (0·8)*
C(1)	593 (8)	5348 (22)	7323 (21)	5·0 (0·4)
C(2)	84 (8)	6120 (20)	8412 (20)	5·3 (0·4)
C(3)	−52 (9)	7755 (26)	7972 (24)	5·9 (0·4)
C(4)	536 (8)	8580 (22)	7225 (23)	4·4 (0·4)
C(5)	1085 (7)	7939 (19)	6876 (19)	3·6 (0·3)
C(6)	1617 (8)	8907 (23)	6174 (22)	5·3 (0·4)
C(7)	1950 (8)	8092 (23)	4704 (22)	4·8 (0·4)
C(8)	2202 (7)	6454 (18)	5222 (19)	3·4 (0·3)
C(9)	1580 (7)	5522 (19)	5669 (19)	4·0 (0·3)
C(10)	1234 (8)	6213 (20)	7249 (20)	4·5 (0·4)
C(11)	1803 (9)	3807 (24)	6064 (24)	5·4 (0·4)
C(12)	2112 (7)	3076 (23)	4457 (23)	5·1 (0·4)
C(13)	2721 (7)	4000 (19)	4010 (20)	3·8 (0·3)
C(14)	2464 (7)	5701 (22)	3621 (19)	4·6 (0·3)
C(15)	3033 (9)	6458 (23)	2763 (23)	5·1 (0·4)
C(16)	3325 (8)	5194 (24)	1681 (22)	5·5 (0·4)
C(17)	2976 (7)	3617 (20)	2207 (21)	4·0 (0·4)
C(18)	3230 (8)	3988 (21)	5470 (23)	5·1 (0·5)*
C(19)	1575 (8)	5997 (27)	9040 (22)	5·7 (0·6)*
C(20)	3439 (7)	2230 (19)	2057 (24)	4·3 (0·5)*
C(21)	3126 (10)	745 (25)	2786 (26)	6·9 (0·7)*
C(22)	3655 (9)	2029 (21)	150 (26)	6·1 (0·6)*
C(23)	4117 (11)	740 (28)	−188 (30)	8·7 (0·8)*
C(24)	4253 (13)	533 (33)	−2155 (30)	10·6 (1·0)*
C(25)	4593 (12)	−852 (33)	−2503 (35)	9·9 (1·0)*
C(26)	4802 (13)	−716 (31)	−4491 (31)	9·7 (1·0)*
C(27)	4190 (15)	−2277 (31)	−2277 (42)	12·0 (1·2)*

* $B_{eq} = \frac{4}{3}\sum_i\sum_j \beta_{ij}\,\mathbf{a}_i.\mathbf{a}_j$.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36017 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Torsional angles* (°) *and asymmetry parameters* (°)

Ring *A*

C(10)–C(1)–C(2)–C(3)	52·1 (2·1)
C(1)–C(2)–C(3)–C(4)	28·2 (2·2)
C(2)–C(3)–C(4)–C(5)	4·7 (2·6)
C(3)–C(4)–C(5)–C(10)	2·6 (2·7)
C(4)–C(5)–C(10)–C(1)	22·6 (2·1)
C(5)–C(10)–C(1)–C(2)	−46·1 (1·8)

$\Delta C_s(1) = 4{\cdot}9$, $\Delta C_s(2) = 29{\cdot}9$, $\Delta C_s(3) = 34{\cdot}4$, $\langle C_s\rangle_A = 23{\cdot}1$
$\Delta C_2(1\text{–}10) = 27{\cdot}6$, $\Delta C_2(2\text{–}1) = 17{\cdot}9$, $\Delta C_2(3\text{–}2) = 45{\cdot}5$, $\langle C_2\rangle_A = 30{\cdot}3$

Ring *B*

C(10)–C(5)–C(6)–C(7)	45·7 (1·9)
C(5)–C(6)–C(7)–C(8)	−54·3 (1·9)
C(6)–C(7)–C(8)–C(9)	61·2 (1·7)
C(7)–C(8)–C(9)–C(10)	−62·4 (1·6)
C(8)–C(9)–C(10)–C(5)	55·2 (1·6)
C(9)–C(10)–C(5)–C(6)	−45·9 (1·8)

$\Delta C_s(5) = 0{\cdot}9$, $\Delta C_s(6) = 11{\cdot}0$, $\Delta C_s(7) = 11{\cdot}7$, $\langle C_s\rangle_B = 7{\cdot}9$
$\Delta C_2(5\text{–}10) = 8{\cdot}8$, $\Delta C_2(6\text{–}5) = 7{\cdot}3$, $\Delta C_2(10\text{–}9) = 16{\cdot}0$, $\langle C_2\rangle_B = 10{\cdot}7$

Ring *C*

C(14)–C(8)–C(9)–C(11)	60·9 (1·5)
C(8)–C(9)–C(11)–C(12)	−60·4 (1·7)
C(9)–C(11)–C(12)–C(13)	62·0 (1·8)
C(11)–C(12)–C(13)–C(14)	−59·5 (1·6)
C(12)–C(13)–C(14)–C(8)	65·0 (1·6)
C(13)–C(14)–C(8)–C(9)	−66·9 (1·5)

$\Delta C_s(8) = 4{\cdot}6$, $\Delta C_s(9) = 4{\cdot}3$, $\Delta C_s(11) = 1{\cdot}7$, $\langle C_s\rangle_C = 3{\cdot}5$
$\Delta C_2(8\text{–}9) = 5{\cdot}1$, $\Delta C_2(14\text{–}8) = 3{\cdot}3$, $\Delta C_2(9\text{–}11) = 5{\cdot}3$, $\langle C_2\rangle_C = 4{\cdot}6$

Ring *D*

C(17)–C(13)–C(14)–C(15)	−48·9 (1·5)
C(13)–C(14)–C(15)–C(16)	35·8 (1·6)
C(14)–C(15)–C(16)–C(17)	−9·3 (1·8)
C(15)–C(16)–C(17)–C(13)	−21·6 (1·7)
C(16)–C(17)–C(13)–C(14)	42·0 (1·4)

Side chain

C(13)–C(17)–C(20)–C(22)	−179·2 (1·4)
C(13)–C(17)–C(20)–C(21)	55·1 (1·9)
C(17)–C(20)–C(22)–C(23)	178·9 (1·6)
C(20)–C(22)–C(23)–C(24)	174·4 (1·7)
C(22)–C(23)–C(24)–C(25)	−169·1 (2·0)
C(23)–C(24)–C(25)–C(26)	−169·7 (2·0)
C(23)–C(24)–C(25)–C(27)	69·8 (2·8)

ORFFE (Busing, Martin & Levy, 1964), a function and error program, and *NUCLS* [J. A. Ibers and R. J. Doedens; a version of Busing, Martin & Levy's (1962) *ORFLS* program].

Discussion. The bond lengths and valence angles are given in Fig. 2 and torsional angles are shown in Table 2. The standard deviations of bond lengths are 0·02 Å at the steroid nucleus, 0·03 Å in the C(20)–C(25) region and 0·04 Å for bonds C(25)–C(26) and C(25)–C(27). The corresponding values for interbond angles are between 1 and 2°. C–C single bonds range from 1·48–1·61 Å with a mean of 1·54 Å. C–Br bond lengths have normal values, but both double bonds (C–C and C–O) are shorter than expected, most likely due to the vinylic influence of Br. The steroid rings *A*, *B*, *C* and *D* are *trans*-fused. The conformation of the six-membered rings may be described by a mirror plane and twofold asymmetry parameters, as defined by Duax & Norton (1975). By inspection of these values (Table 2) it may be concluded that the conformations of the *B* and *C* rings are distorted chair and chair respectively. The *A* ring has a distorted sofa conformation. The shape of cyclopentane ring *D* is characterized by parameters Δ and φ_m, *i.e.* the phase angle and maximal torsion angle as given by Altona, Geise & Romers (1968), and by the torsional angles (Table 2). φ_m and Δ are −49·6 and 15° respectively, showing that the *D*-ring conformation is intermediate between a half chair and a C(13) envelope. The conformation of the C(17) side chain is approximately fully extended. The packing of molecules in the unit cell is shown in Fig. 3. The arrangement of the steroids in the crystal is in a 'head-to-tail' and 'tail-to-tail' fashion and the greatest

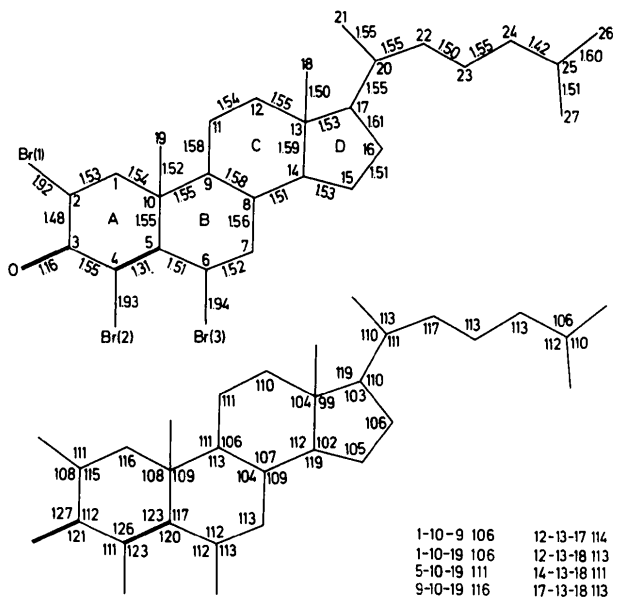

Fig. 2. Bond distances (Å) and bond angles (°).

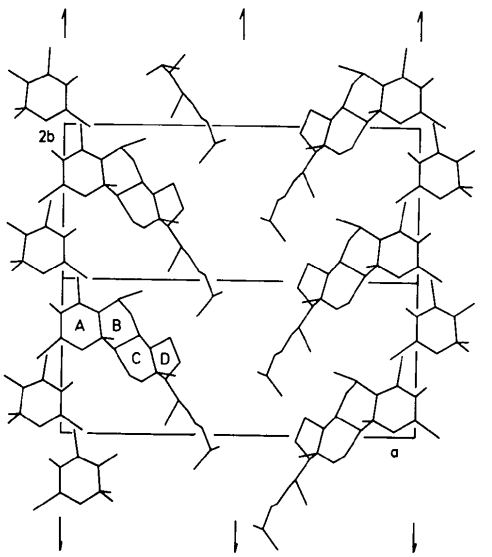

Fig. 3. The molecular packing as viewed down **c**.

Table 3. *Intermolecular distances less than* 4 Å

Br(1)–Br(2)^{iii}	3·726 (3)	O–C(1)^{iii}	3·81 (2)
Br(1)–O^{iv}	3·90 (1)	O–C(2)^{iii}	3·57 (2)
Br(1)–C(2)^{iv}	3·76 (2)	O–C(12)^{iii}	3·81 (2)
Br(1)–C(4)^{iv}	3·66 (2)	O–C(19)^{iii}	3·83 (2)
Br(1)–C(6)^{iv}	3·91 (2)	C(6)–C(12)^{i}	3·99 (3)
Br(1)–C(7)^{iv}	3·74 (2)	C(7)–C(21)^{i}	3·71 (3)
Br(2)–C(2)^{iii}	3·69 (2)	C(14)–C(19)^{ii}	3·89 (2)
Br(3)–C(11)^{i}	3·99 (2)	C(15)–C(21)^{i}	3·72 (3)
Br(3)–C(22)^{i}	3·95 (2)		

Symmetry code

None	x, y, z	(iii)	$-x, y + \frac{1}{2}, -z + 2$
(i)	$x, y + 1, z$	(iv)	$-x, (y + \frac{1}{2}) - 1, -z + 2$
(ii)	$x, y, -z + 1$		

number of closest intermolecular contacts (Table 3) are through substituents of the *A* rings, but no distances less than 4 Å are found in the regions of neighbouring distal parts of the side chains. This partial lack of packing is probably one of the reasons for the relatively high mobility of the terminal side-chain atoms. Therefore, it seems that in the crystal structure of this cholestane derivative the tail or a part of the tail is in a state similar to a semi-liquid, as has previously been found in some other cholestane derivatives (Craven, 1970; Craven & DeTitta, 1976; Chandross & Bordner, 1977).

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α,α-Bis(*p*-chlorophenyl)-3-pyridinemethanol (Parinol)

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Abstract. $C_{18}H_{13}Cl_2NO$, $M_r = 330$, orthorhombic, $Pna2_1$, $a = 11{\cdot}557$ (1), $b = 13{\cdot}958$ (2), $c = 9{\cdot}652$ (1) Å, $Z = 4$, $D_x = 1{\cdot}41$ Mg m^{-3}, $F(000) = 680$, μ(Cu $K\alpha$) = 3·72 mm^{-1}; $R = 0{\cdot}053$ for 1305 observed reflections. The molecules are linked by a single intermolecular hydrogen bond (N···O, 2·746 Å) between the pyridine N and the hydroxyl O. The pyridine ring is approximately perpendicular to the plane of C–C–O. The dihedral angle between the planes of the benzene ring is 80·7°, giving torsion angles [C(8–7–13–14)] and [C(2–1–13–14)] down the ring-C to α-C vectors of −87·0 (3) and +38·7 (3)° respectively.

Introduction. Parinol is the common name for α,α-bis(*p*-chlorophenyl)-3-pyridinemethanol which was introduced under the trade name Parnon as a commercial fungicide (EL-241) by Eli Lilly & Co. (Thayer, Ford & Hall, 1967). The structure–fungicidal-activity relationships for parinol and other 3-pyridine alcohols and alkanes have been reported (Brown, Whaley, Taylor & Van Heynigen, 1967; Whaley & Taylor, 1970). Parinol possesses structural features in common with the insecticide *p,p'*-DDT (DeLacy & Kennard, 1972), the central trichloroethane moiety being replaced by the 3-pyridylmethanol group. Loss in insecticidal activity results when bulky groups are introduced into the 2-position of the ethyl group in *p,p'*-DDT, *e.g.* chlorine [1,1,1,2-tetrachloro-2,2-bis(*p*-chlorophenyl)-ethane (Hovmöller, Smith & Kennard, 1978)] or hydroxyl [1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethanol (dicofol) (Smith, Kennard & White, 1978)]. The structure was determined in order to compare the effect of both the pyridyl and hydroxyl groups on the relative conformational aspects of the *p*-chlorophenyl groups and to observe the effects hydrogen-bonding associations may have on the mode of packing of the molecules in the solid state. This work is part of a structural study of DDT-like compounds. The previous structure in this series was 1,1-bis(*p*-methoxyphenyl)-2,2-dimethylpropane (Smith, Kennard & Palm, 1980).

Colourless crystals, m.p. 452–453 K, were grown from a mixture of hexane and acetone. Preliminary X-ray data (*0kl*, $k + l$ = odd; *h0l*, h = odd) were consistent for either space group *Pnam* or $Pna2_1$, the latter being confirmed by successful structure solution and refinement. 1305 reflections with $I > 2{\cdot}5\sigma(I)$ were considered observed out of 1475 unique reflections collected from one crystal (0·05 × 0·28 × 0·18 mm) mounted along the *a* axis in the counter aperture of a Philips PW 1100 four-circle diffractometer ($2\theta_{max}$ = 134°; graphite-monochromatized Cu $K\alpha$ radiation) using an $\omega/2\theta$ scanning mode with a fixed scan width of 1·6°. The data were corrected for absorption but not for extinction.

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