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Acta Cryst. (1987). C**43**, 967–968

Structure of 2,4-Dibromo-10β,17β-dihydroxy-1,4-estradien-3-one

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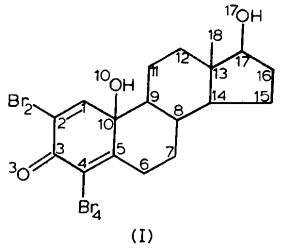
(*Received* 20 *June* 1986; *accepted* 12 *December* 1986)

Abstract. $C_{18}H_{22}Br_2O_3$, $M_r = 446{\cdot}19$, tetragonal, $P4_1$, $a = 9{\cdot}4634\ (3)$, $c = 20{\cdot}0447\ (15)$ Å, $V = 1795{\cdot}1\ (3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}650$ Mg m^{-3}, λ(Cu $K\alpha$) $= 1{\cdot}5418$ Å, $\mu = 5{\cdot}875$ mm^{-1}, $F(000) = 896$, room temperature, final $R = 4{\cdot}1\%$ for 1826 reflections. The hydroxyl group at C(10) exists in a β configuration. The hydroxyl groups at C(17) and C(10) and the oxygen at C(3) form two intermolecular hydrogen bonds.

Introduction. The title compound (I) was synthesized in connection with the development of a new method of adding a hydroxyl to the C(10) position in steroids. The compound was derived from 2,4-dibromoestradiol by treatment with nitric acid. Since the configuration at C(10) was uncertain, an X-ray crystal structure analysis of the product was undertaken.



(I)

Experimental. Recrystallization from methanol, single crystal $0{\cdot}30 \times 0{\cdot}30 \times 0{\cdot}68$ mm. The unit-cell parameters were refined from accurately measured 2θ values of 25 reflections from the range $71 < 2\theta < 84°$. Intensities of 2343 unique reflections having $\theta < 77°$ ($0 \le h \le 11$, $0 \le k \le 11$, $-25 \le l \le 1$) measured on an Enraf–Nonius CAD-4 diffractometer using Cu $K\alpha$ radiation. Four standard reflections ($71\bar{1}$, $3,1,\bar{15}$, $44\bar{9}$, $17\bar{3}$) varied in intensity by $\le 5\%$ during the data collection. Direct methods using *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) revealed positions of all non-hydrogen atoms. The positional and anisotropic displacement parameters of all non-hydrogen atoms were refined by full-matrix least squares on F using the 1826 reflections for which $I > 2{\cdot}0\sigma(I)$. Hydrogens found from ΔF maps and refined with assigned isotropic temperature parameters of their bonding partners except those at C(15), C(16) and C(18) which were placed at calculated positions and not refined. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974) and anomalous-dispersion corrections for non-hydrogen atoms from Cromer & Liberman (1970). Final $R = 4{\cdot}1\%$, $wR = 5{\cdot}4\%$, $S = 2{\cdot}523$ for observed reflections, $w = 1/\sigma_F^2$, $(\Delta/\sigma)_{max} = 0{\cdot}38$. Final difference maps showed strongest peak (trough) of $+0{\cdot}60$ ($-0{\cdot}70$) e Å^{-3}. No corrections for absorption or secondary extinction.

Discussion. The atomic positional parameters and equivalent thermal parameters for non-hydrogen atoms are given in Table 1.* A stereoscopic view of the molecule showing the molecular conformation is given in Fig. 1. The bond distances and angles listed in Table 2 do not deviate significantly from average values observed in other steroids (Griffin, Duax & Weeks, 1984). The Br—C distances are close to those found in 2,4-dibromoestradiol (Cody, DeJarnette, Duax & Norton, 1971).

The crystal structure determination of the compound proved that the hydroxyl at the C(10) position is in

* Lists of torsion angles, structure factors, anisotropic thermal parameters and hydrogen parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43642 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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the β orientation. The *A* ring is planar, rings *B* and *C* have chair conformations and the *D* ring has a 13β-envelope conformation.

Table 1. *Fractional atomic coordinates* (×10⁵) *and equivalent isotropic thermal parameters* (Å² × 10²) *with e.s.d.'s in parentheses*

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

	x	*y*	*z*	B_{eq}
C(1)	90032 (57)	34615 (47)	−6731 (27)	340 (10)
C(2)	91512 (63)	25278 (47)	−1699 (29)	375 (12)
C(3)	79701 (70)	20078 (51)	2337 (29)	398 (12)
C(4)	65747 (56)	26329 (43)	679 (25)	335 (10)
C(5)	63624 (55)	35520 (43)	−4453 (27)	330 (10)
C(6)	49626 (53)	41561 (54)	−6402 (38)	415 (14)
C(7)	49888 (50)	57803 (49)	−6072 (28)	336 (11)
C(8)	62100 (44)	63642 (41)	−10216 (23)	267 (8)
C(9)	76284 (45)	57436 (39)	−7679 (23)	263 (8)
C(10)	75906 (50)	41079 (42)	−8550 (24)	291 (9)
C(11)	89441 (50)	63991 (45)	−10956 (26)	317 (10)
C(12)	89095 (48)	80174 (46)	−11062 (27)	318 (10)
C(13)	75385 (45)	85501 (40)	−14168 (22)	262 (8)
C(14)	63025 (45)	79780 (41)	−9922 (25)	277 (9)
C(15)	50221 (53)	88319 (51)	−12209 (37)	395 (12)
C(16)	56592 (63)	102967 (53)	−14074 (40)	429 (14)
C(17)	72565 (54)	101302 (40)	−13239 (26)	321 (10)
C(18)	74427 (70)	81665 (48)	−21587 (27)	359 (12)
Br(2)	109468 (9)	17241 (8)	−226	577 (2)
Br(4)	50714 (9)	19245 (9)	5620 (6)	599 (2)
O(3)	81004 (65)	10974 (53)	6537 (30)	593 (14)
O(10)	73470 (45)	38380 (41)	−15471 (19)	351 (8)
O(17)	80009 (47)	110549 (33)	−17739 (23)	393 (9)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

C(1)–C(2)	1·348 (7)	C(8)–C(14)	1·531 (5)
C(1)–C(10)	1·515 (7)	C(9)–C(10)	1·558 (5)
C(2)–C(3)	1·465 (8)	C(9)–C(11)	1·538 (6)
C(2)–Br(2)	1·885 (6)	C(10)–O(10)	1·429 (6)
C(3)–C(4)	1·485 (8)	C(11)–C(12)	1·532 (6)
C(3)–O(3)	1·211 (8)	C(12)–C(13)	1·525 (6)
C(4)–C(5)	1·362 (7)	C(13)–C(14)	1·545 (6)
C(4)–Br(4)	1·859 (5)	C(13)–C(17)	1·530 (5)
C(5)–C(6)	1·495 (7)	C(13)–C(18)	1·533 (7)
C(5)–C(10)	1·517 (7)	C(14)–C(15)	1·527 (7)
C(6)–C(7)	1·539 (7)	C(15)–C(16)	1·557 (7)
C(7)–C(8)	1·527 (7)	C(16)–C(17)	1·529 (8)
C(8)–C(9)	1·551 (6)	C(17)–O(17)	1·441 (6)

C(2)–C(1)–C(10)	122·4 (4)	C(1)–C(10)–C(9)	110·7 (3)
C(1)–C(2)–C(3)	123·6 (4)	C(1)–C(10)–O(10)	107·7 (3)
C(1)–C(2)–Br(2)	118·4 (4)	C(5)–C(10)–C(9)	107·5 (3)
C(3)–C(2)–Br(2)	117·8 (4)	C(5)–C(10)–O(10)	109·9 (3)
C(2)–C(3)–C(4)	114·9 (4)	C(9)–C(10)–O(10)	106·9 (3)
C(2)–C(3)–O(3)	123·0 (4)	C(9)–C(11)–C(12)	113·1 (3)
C(4)–C(3)–O(3)	122·0 (4)	C(11)–C(12)–C(13)	110·8 (3)
C(3)–C(4)–C(5)	123·7 (4)	C(12)–C(13)–C(14)	107·7 (3)
C(3)–C(4)–Br(4)	114·7 (3)	C(12)–C(13)–C(17)	114·9 (3)
C(5)–C(4)–Br(4)	121·3 (3)	C(12)–C(13)–C(18)	111·6 (3)
C(4)–C(5)–C(6)	124·9 (4)	C(14)–C(13)–C(17)	98·2 (3)
C(4)–C(5)–C(10)	121·1 (4)	C(14)–C(13)–C(18)	114·0 (3)
C(6)–C(5)–C(10)	113·9 (4)	C(17)–C(13)–C(18)	109·8 (3)
C(5)–C(6)–C(7)	110·9 (4)	C(8)–C(14)–C(13)	111·8 (3)
C(6)–C(7)–C(8)	110·5 (4)	C(8)–C(14)–C(15)	118·1 (3)
C(7)–C(8)–C(9)	109·9 (3)	C(13)–C(14)–C(15)	104·5 (3)
C(7)–C(8)–C(14)	112·5 (3)	C(14)–C(15)–C(16)	103·6 (4)
C(9)–C(8)–C(14)	108·4 (3)	C(15)–C(16)–C(17)	105·4 (4)
C(8)–C(9)–C(10)	108·6 (3)	C(13)–C(17)–C(16)	105·1 (4)
C(8)–C(9)–C(11)	114·1 (3)	C(13)–C(17)–O(17)	115·6 (3)
C(10)–C(9)–C(11)	111·8 (3)	C(16)–C(17)–O(17)	110·6 (4)
C(1)–C(10)–C(5)	113·9 (3)		

Fig. 1. A stereodrawing of the molecule. Thermal ellipsoids are at 50% probability for non-hydrogen atoms (*ORTEP*; Johnson, 1965).

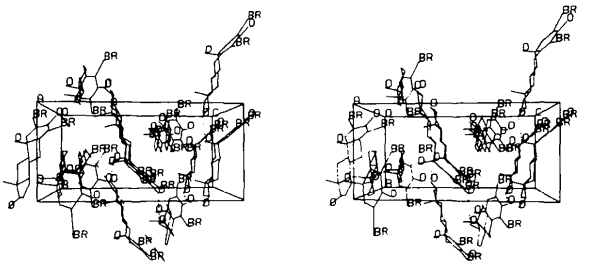

Fig. 2. Stereoscopic packing diagram of the crystal structure down [100].

The molecules in the crystal are connected by means of hydrogen bonds formed between hydroxyl groups at C(17) and C(10) and oxygen atoms at the C(3) position (Fig. 2):

Donor (*D*)	Acceptor (*A*)	D···*A* (Å)	D–H (Å)	*A*···H (Å)	*D*–H···*A* (°)
O(17)	O(3^{i})	3·041 (7)	1·04 (7)	2·12 (7)	146 (5)
O(10)	O(17^{ii})	2·743 (5)	0·76 (6)	1·99 (5)	169 (5)

Symmetry code (i) $1+y, 2-x, z-\frac{1}{4}$; (ii) $-x, -y-1, \frac{1}{2}+z$.

The first of these hydrogen bonds, between O(17) and O(3), links the steroid molecules into an infinite coil running parallel to the *c* axis. Interdigitated coils are linked together by the second hydrogen bond from O(10) to O(17).

This research was supported by Project MR.I.9 from the Polish Academy of Sciences and by Grant No. AM-26546 from the National Institute of Arthritis, Diabetes and Digestive and Kidney Diseases.

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