Table 2. *Bond lengths* (Å) *for non-hydrogen atoms with estimated standard deviations in parentheses*

C(1)–C(2)	1·394 (8)	C(9)–C(10)	1·515 (6)
C(1)–C(10)	1·381 (6)	C(9)–C(11)	1·529 (8)
C(2)–C(3)	1·379 (9)	C(11)–C(12)	1·499 (7)
C(3)–C(4)	1·366 (6)	C(12)–C(13)	1·517 (6)
C(3)–O(3)	1·380 (6)	C(13)–C(14)	1·539 (7)
C(4)–C(5)	1·383 (7)	C(13)–C(17)	1·524 (6)
C(5)–O(6)	1·370 (5)	C(13)–C(18)	1·551 (7)
C(5)–C(10)	1·388 (8)	C(14)–C(15)	1·544 (5)
O(6)–C(7)	1·455 (6)	C(15)–C(16)	1·516 (9)
C(7)–C(8)	1·512 (8)	C(16)–C(17)	1·481 (7)
C(7)–O(7)	1·389 (5)	C(17)–O(17)	1·217 (7)
C(8)–C(9)	1·534 (6)	O(3)–C(19)	1·425 (7)
C(8)–C(14)	1·540 (5)		

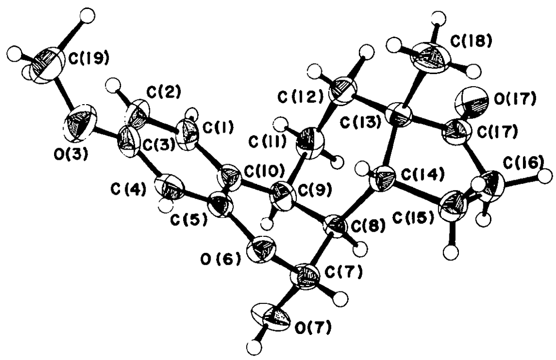

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the molecule. Thermal ellipsoids for non-hydrogen atoms are scaled to 50% probability, and H atoms are represented as spheres of radius 0·1 Å.

The 7-hydroxy group exhibits an O–H distance of 1·00 (8) Å and, in addition, the H atom forms a contact at 1·82 (7) Å with O(17) of a neighboring ($x,\frac{1}{2} - y,-\frac{1}{2} + z$) molecule, producing a chain of hydrogen-bonded molecules. The O(7)–H(O7)···O(17) angle is

Table 3. *Bond angles* (°) *for the non-hydrogen atoms with estimated standard deviations in parentheses*

C(2)–C(1)–C(10)	122·9 (6)	C(1)–C(10)–C(9)	122·7 (5)
C(1)–C(2)–C(3)	118·3 (4)	C(5)–C(10)–C(9)	120·6 (3)
C(2)–C(3)–C(4)	120·4 (5)	C(9)–C(11)–C(12)	111·8 (5)
C(2)–C(3)–O(3)	122·7 (4)	C(11)–C(12)–C(13)	111·8 (4)
C(4)–C(3)–O(3)	116·9 (5)	C(12)–C(13)–C(14)	115·9 (3)
C(3)–C(4)–C(5)	120·1 (6)	C(12)–C(13)–C(17)	112·7 (4)
C(4)–C(5)–O(6)	115·7 (5)	C(12)–C(13)–C(18)	110·9 (4)
C(4)–C(5)–C(10)	121·6 (4)	C(14)–C(13)–C(17)	102·5 (3)
O(6)–C(5)–C(10)	122·7 (4)	C(14)–C(13)–C(18)	110·0 (5)
C(5)–O(6)–C(7)	117·0 (4)	C(17)–C(13)–C(18)	104·0 (3)
O(6)–C(7)–C(8)	110·9 (3)	C(8)–C(14)–C(13)	114·5 (4)
O(6)–C(7)–O(7)	109·4 (3)	C(8)–C(14)–C(15)	110·3 (3)
C(8)–C(7)–O(7)	108·6 (5)	C(13)–C(14)–C(15)	103·4 (3)
C(7)–C(8)–C(9)	108·2 (3)	C(14)–C(15)–C(16)	105·1 (4)
C(7)–C(8)–C(14)	111·1 (4)	C(15)–C(16)–C(17)	105·7 (3)
C(9)–C(8)–C(14)	114·6 (3)	C(13)–C(17)–C(16)	110·3 (4)
C(8)–C(9)–C(10)	110·6 (4)	C(13)–C(17)–O(17)	123·4 (4)
C(8)–C(9)–C(11)	110·0 (3)	C(16)–C(17)–O(17)	126·3 (4)
C(10)–C(9)–C(11)	113·6 (4)	C(3)–O(3)–C(19)	117·6 (5)
C(1)–C(10)–C(5)	116·6 (4)		

153 (5)°. No other short intermolecular contacts were observed.

References

CORFIELD, P. W. R., DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 197–204.

FINDLAY, J. A. & MEBE, P. (1979). *Can. J. Chem.* Submitted.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

MEBE, P. (1978). *Total Synthesis of Miroestrol Analogues – 6-Oxasteroids*. PhD Thesis, Univ. of New Brunswick.

STEWART, J. M. (1976). Editor. The XRAY system – version of 1976. Tech. Rep. TR-446. Computer Science Center, Univ. of Mayland, College Park, Maryland.

TAYLOR, N. E., HODGKIN, D. C. & ROLLETT, J. S. (1960). *J. Chem. Soc.* pp. 3685–3695.

Acta Cryst. (1980). B**36**, 491–493

3-Methoxy-6-oxaestra-1,3,5(10)-triene-7,17-dione 17-(Ethylene Acetal)

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(*Received* 3 *August* 1979; *accepted* 22 *October* 1979)

Abstract. $C_{20}H_{24}O_5$, M_r = 344·4, triclinic, $P\bar{1}$, a = 14·540 (6), b = 6·393 (3), c = 9·820 (5) Å, α = 107·19 (3), β = 97·89 (3), γ = 95·26 (3)°, V = 855 (1) Å^3, Z = 2, ρ_x = 1·34 Mg m^{-3}, $F(000)$ = 368, λ(Mo $K\alpha$) = 0·71069 Å. Intensities for 1593 (1264 observed) unique reflections were collected on a diffractometer. A full-matrix least-squares refinement gave a final R of 0·055. There are no short intermolecular contacts.

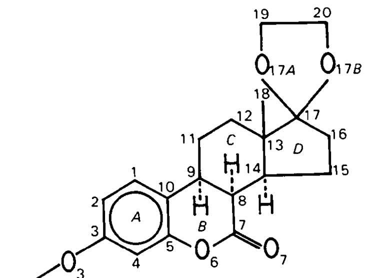
0567-7408/80/020491-03$01.00

Table 1. *Fractional atomic coordinates* ($\times 10^4$ *for the non-hydrogen atoms*, $\times 10^3$ *for* H; *e.s.d.'s in parentheses*) *and isotropic thermal parameter values* ($U_{eq} \times 10^3$ *for non-hydrogen atoms*, $U \times 10^2$ *for* H; *e.s.d.'s for U in parentheses*)

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{23}\cos\alpha + 2U_{13}\cos\beta + 2U_{12}\cos\gamma).$$

	x	y	z	U_{eq}/U (Å^2)
C(1)	4024 (3)	−2837 (8)	7209 (5)	40
C(2)	3095 (4)	−2537 (9)	7158 (5)	41
C(3)	2864 (3)	−389 (8)	7542 (5)	34
C(4)	3554 (3)	1383 (8)	7951 (5)	38
C(5)	4479 (3)	991 (7)	7957 (5)	34
C(7)	6070 (3)	2858 (9)	8657 (5)	36
C(8)	6379 (3)	664 (7)	8706 (5)	31
C(9)	5756 (3)	−1323 (8)	7602 (5)	34
C(10)	4748 (3)	−1068 (7)	7604 (4)	32
C(11)	5988 (3)	−1788 (10)	6073 (6)	45
C(12)	7031 (3)	−2021 (9)	6040 (6)	43
C(13)	7657 (3)	6 (7)	7092 (5)	31
C(14)	7414 (3)	458 (8)	8603 (5)	33
C(15)	8213 (3)	2174 (10)	9606 (6)	45
C(16)	9075 (3)	1650 (10)	8850 (6)	46
C(17)	8711 (3)	−196 (8)	7455 (5)	39
C(18)	7593 (4)	1984 (10)	6508 (7)	44
C(19)	9537 (5)	−3153 (12)	6955 (8)	68
C(20)	9533 (5)	−2187 (11)	5758 (8)	64
C(21)	1667 (4)	1908 (10)	8003 (8)	60
O(3)	1924 (2)	−246 (5)	7439 (3)	47
O(6)	5130 (2)	2880 (5)	8293 (4)	47
O(7)	6566 (2)	4585 (6)	8969 (4)	53
O(17*A*)	8799 (2)	−2309 (5)	7651 (4)	53
O(17*B*)	9236 (2)	−90 (5)	6347 (4)	52
H(1)	417 (3)	−435 (8)	696 (4)	6 (1)
H(2)	259 (3)	−381 (7)	684 (4)	4 (1)
H(4)	344 (2)	287 (6)	825 (4)	5 (1)
H(8)	629 (2)	69 (5)	978 (4)	2 (1)
H(9)	587 (2)	−255 (6)	788 (4)	3 (1)
H(11*A*)	555 (3)	−326 (8)	533 (5)	6 (1)
H(11*B*)	581 (3)	−79 (7)	562 (4)	4 (1)
H(12*A*)	712 (3)	−230 (6)	501 (5)	4 (1)
H(12*B*)	717 (2)	−333 (6)	633 (4)	3 (1)
H(14)	749 (2)	−80 (6)	885 (4)	3 (1)
H(15*A*)	829 (3)	233 (8)	1074 (6)	8 (2)
H(15*B*)	810 (3)	375 (8)	973 (5)	6 (2)
H(16*A*)	955 (3)	116 (7)	944 (5)	5 (1)
H(16*B*)	936 (3)	305 (8)	866 (5)	7 (2)
H(18*A*)	689 (4)	229 (8)	625 (5)	9 (2)
H(18*B*)	781 (3)	171 (8)	562 (6)	7 (2)
H(18*C*)	796 (3)	338 (9)	725 (5)	7 (2)
H(19*A*)	1027 (7)	−254 (16)	767 (11)	24 (5)
H(19*B*)	939 (4)	−470 (10)	667 (6)	10 (2)
H(20*A*)	1009 (4)	−193 (10)	541 (7)	12 (2)
H(20*B*)	901 (4)	−336 (9)	469 (6)	10 (2)
H(21*A*)	200 (3)	268 (7)	913 (5)	6 (1)
H(21*B*)	180 (5)	286 (12)	719 (8)	15 (3)
H(21*C*)	99 (4)	142 (8)	765 (5)	8 (2)

Introduction. The title compound (I), a key intermediate in the successful total synthesis of analogues of miroestrol (Taylor, Hodgkin & Rollett, 1960), a very potent estrogen of natural origin, was subjected to structural study to establish the ring-junction stereochemistry. Revelation of the *cis–syn–trans B/C–C/D* ring system *via* this study provided a firm basis for further manipulation and the successful realization of several steroidal analogues possessing precisely defined ring-junction stereochemistry and featuring the novel 6-oxa-7-ene system (Mebe, 1978). These compounds exhibit interesting estrogenic activity and will be reported elsewhere (Findlay & Mebe, 1979).



(I)

Crystallographic data were measured on a specimen crystal of dimensions 0·56 × 0·22 × 0·04 mm using a Picker FACS-I diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Preliminary photographic work had shown the crystal to be triclinic. The lattice parameters were refined by a least-squares fit of cell dimensions and an orientation matrix to the diffractometer settings for 12 well centered reflections in the interval 30° < 2θ < 33°. Of the 1593 independent reflections measured in the range 2θ < 40°, 329 (20·7%) were considered unobserved [$I < 3\sigma(I)$] and were not included in subsequent calculations.

Data reduction and structure refinement utilized the XRAY 76 program package (Stewart, 1976). Initial positional parameters for non-hydrogen atoms were determined using the *MULTAN* system of direct-methods programs (Germain, Main & Woolfson, 1971). The space group was assumed to be the centrosymmetric $P\bar{1}$ on the basis of the distribution of the normalized structure factors. The H atoms were located on a difference electron density map prepared at an intermediate stage of least-squares refinement of

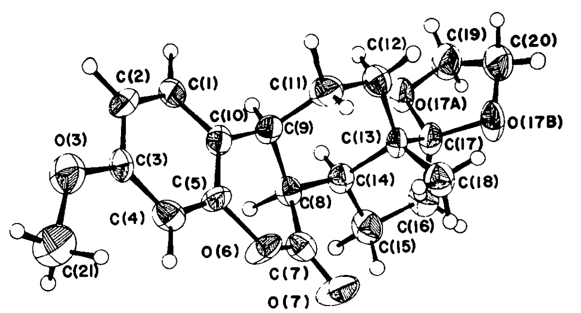


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the molecule. Thermal ellipsoids for non-hydrogen atoms are scaled to 50% probability, and H atoms are represented as spheres of radius 0·1 Å.

Table 2. *Bond lengths* (Å) *for non-hydrogen atoms with estimated standard deviations in parentheses*

C(1)–C(2)	1·377 (7)	C(11)–C(12)	1·542 (7)
C(1)–C(10)	1·396 (6)	C(12)–C(13)	1·520 (6)
C(2)–C(3)	1·398 (7)	C(13)–C(14)	1·522 (7)
C(3)–C(4)	1·365 (6)	C(13)–C(17)	1·551 (6)
C(3)–O(3)	1·369 (5)	C(13)–C(18)	1·540 (9)
C(4)–C(5)	1·390 (6)	C(14)–C(15)	1·528 (6)
C(5)–O(6)	1·390 (5)	C(15)–C(16)	1·555 (8)
C(5)–C(10)	1·367 (6)	C(16)–C(17)	1·511 (6)
O(6)–C(7)	1·367 (6)	C(17)–O(17*A*)	1·434 (6)
C(7)–C(8)	1·523 (7)	C(17)–O(17*B*)	1·426 (6)
C(7)–O(7)	1·194 (6)	O(17*A*)–C(19)	1·413 (8)
C(8)–C(9)	1·522 (5)	O(17*B*)–C(20)	1·426 (7)
C(8)–C(14)	1·538 (6)	C(19)–C(20)	1·480 (12)
C(9)–C(10)	1·489 (6)	O(3)–C(21)	1·428 (7)
C(9)–C(11)	1·533 (8)		

structural parameters. In the final cycles of full-matrix least-squares refinement, positional parameters for all atoms, anisotropic thermal vibration parameters for the non-hydrogen atoms and isotropic thermal vibration parameters for the H atoms were varied. Using a weighting scheme of $w = 1/\sigma^2(F)$ where $\sigma(F)$ is directly derived from $\sigma(I)$ (Corfield, Doedens & Ibers, 1967), refinement converged to $R = 0{\cdot}055$, $R_w = 0{\cdot}062$, where $R = \sum||F_o| - |F_c||/\sum|F_o|$, for the 1264 reflections. The function minimized by the procedure was $\sum w(|F_o| - |F_c|)^2$. The average shift/error for the final cycle was 0·050 with a maximum of 0·459 associated with the y coordinate of H(4). The atomic parameters are listed in Table 1.* A ΔF synthesis showed a maximum electron density of 0·18 e Å^{-3} and a minimum electron density of –0·31 e Å^{-3}, indicating no misplaced or uncounted atoms.

Discussion. The crystallographically observed structure of the molecule is shown in Fig. 1. Intramolecular bond lengths and angles, together with estimated standard deviations, are given in Tables 2 and 3 respectively. None of the observed bond distances or angles are significantly different from expected values for (I). No anomalous value was observed amongst the

* Lists of structure factors, thermal parameters and least-squares-plane data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34864 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond angles* (°) *for non-hydrogen atoms with estimated standard deviations in parentheses*

C(2)–C(1)–C(10)	122·4 (5)	C(11)–C(12)–C(13)	110·8 (4)
C(1)–C(2)–C(3)	119·3 (4)	C(12)–C(13)–C(14)	110·6 (4)
C(2)–C(3)–C(4)	120·0 (4)	C(12)–C(13)–C(17)	116·9 (4)
C(2)–C(3)–O(3)	115·3 (4)	C(12)–C(13)–C(18)	109·6 (4)
C(4)–C(3)–O(3)	124·6 (4)	C(14)–C(13)–C(17)	98·8 (3)
C(3)–C(4)–C(5)	118·5 (4)	C(14)–C(13)–C(18)	113·2 (4)
C(4)–C(5)–O(6)	114·7 (4)	C(17)–C(13)–C(18)	107·5 (4)
C(4)–C(5)–C(10)	124·1 (4)	C(8)–C(14)–C(13)	115·5 (4)
O(6)–C(5)–C(10)	121·1 (4)	C(8)–C(14)–C(15)	122·1 (4)
C(5)–O(6)–C(7)	122·1 (4)	C(13)–C(14)–C(15)	105·4 (4)
O(6)–C(7)–C(8)	116·9 (4)	C(14)–C(15)–C(16)	103·5 (4)
O(6)–C(7)–O(7)	116·7 (5)	C(15)–C(16)–C(17)	106·2 (4)
C(8)–C(7)–O(7)	126·3 (4)	C(13)–C(17)–C(16)	104·9 (4)
C(7)–C(8)–C(9)	112·8 (4)	C(13)–C(17)–O(17*A*)	109·3 (4)
C(7)–C(8)–C(14)	115·5 (4)	C(13)–C(17)–O(17*B*)	114·5 (4)
C(9)–C(8)–C(14)	109·8 (4)	C(16)–C(17)–O(17*A*)	110·8 (4)
C(8)–C(9)–C(10)	110·6 (4)	C(16)–C(17)–O(17*B*)	111·9 (4)
C(8)–C(9)–C(11)	113·2 (4)	O(17*A*)–C(17)–O(17*B*)	105·6 (4)
C(10)–C(9)–C(11)	111·1 (4)	C(17)–O(17*A*)–C(19)	107·7 (5)
C(1)–C(10)–C(5)	115·7 (4)	C(17)–O(17*B*)–C(20)	109·1 (5)
C(1)–C(10)–C(9)	124·1 (4)	O(17*A*)–C(19)–C(20)	104·2 (6)
C(5)–C(10)–C(9)	120·2 (4)	O(17*B*)–C(20)–C(19)	102·8 (5)
C(9)–C(11)–C(12)	112·3 (4)	C(3)–O(3)–C(21)	116·7 (3)

final thermal parameters, whose principal values were in the range 23 – 117 × 10^{-3} Å^2. The presence of ring *A* requires formally that atoms C(1), C(2), C(3), C(4), C(5), C(9), C(10), O(3) and O(6) be coplanar; this is found to be so, the maximum deviation from the plane being 0·04 (1) Å at C(4).

After refinement, the 24 C–H bond distances all lay in the range 0·92–1·20 Å with an average distance of 1·02 Å. No short intermolecular contacts were observed.

References

Corfield, P. W. R., Doedens, R. J. & Ibers, J. A. (1967). *Inorg. Chem.* **6**, 197–204.

Findlay, J. A. & Mebe, P. (1979). *Can. J. Chem.* Submitted.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Mebe, P. (1978). *Total Synthesis of Miroestrol Analogues – 6-Oxasteroids*. PhD Thesis, Univ. of New Brunswick.

Stewart, J. M. (1976). Editor. The XRAY system – version of 1976. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Taylor, N. E., Hodgkin, D. C. & Rollett, J. S. (1960). *J. Chem. Soc.* pp. 3685–3695.