

Fig. 1. Crystal structure of TMADP.H<sub>2</sub>O. Hydrogen bonds are drawn as broken lines (Johnson, 1976).

The structure shown in Fig. 1 can be described as follows: H<sub>2</sub>PO<sub>4</sub><sup>-</sup> chains along the *c* axis are formed with PO<sub>4</sub> tetrahedra connected to each other by two H bonds [O(3)—H(1)···O(1<sup>i</sup>) and O(4<sup>i</sup>)—H(2<sup>i</sup>)···O(2)]; two other H bonds [O(5)—H(4)···O(1) and O(5<sup>ii</sup>)—H(3<sup>ii</sup>)···O(2)] between adjacent H<sub>2</sub>PO<sub>4</sub><sup>-</sup> chains are also formed with water molecules. Consequently a two-dimensional network of H bonds is constructed; there are no H bonds between the networks. Bulky N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup> ions exist in the hollow space of the network. As shown in Table 3, the H bonds along the chain are strong and the interchain H bonds weak according to the criterion of O—O distances less than or greater than 2.7 Å (Brown, 1976).

Following Baur (1974), the distortion indices (DI's) related to a PO<sub>4</sub> tetrahedron have been calculated for

P—O distances, O—P—O angles and O—O distances: DI(TO) = 0.021 (0.017), DI(OTO) = 0.021 (0.025) and DI(OO) = 0.007 (0.011); the average values given by Baur (1974) for several acidic orthophosphates are shown in parentheses. All the DI's are zero for a regular PO<sub>4</sub> tetrahedron.

The arrangement of C atoms around N in the N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup> ion is almost ideally tetrahedral. The N—C lengths range from 1.476 (1) to 1.488 (1) Å, and the C—N—C angles from 108.77 (7) to 110.9 (1)° with average values of 1.483 (1) Å and 109.47 (8)° respectively (Table 2).

The experiment and analysis were carried out at the Center of Advanced Instrumental Analysis, Kyushu University.

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## Dimethyl 3,3-Dimethyl-2,4,7-trioxa-*cis*-bicyclo[3.3.0]octane-*exo*-6,*exo*-8-dicarboxylate

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(Received 21 October 1986; accepted 16 December 1986)

**Abstract.** C<sub>11</sub>H<sub>16</sub>O<sub>7</sub>, *M<sub>r</sub>* = 260.2, monoclinic, *P*2<sub>1</sub>/*n*, *a* = 13.724 (4), *b* = 6.543 (2), *c* = 14.507 (3) Å, β = 102.99 (2)°, *U* = 1269 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.36 g cm<sup>-3</sup>, Mo *K*α radiation, λ = 0.71069 Å,

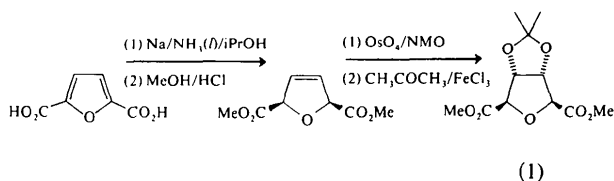
μ(Mo *K*α) = 1.1 cm<sup>-1</sup>, *F*(000) = 552, *T* = 298 K, *R* = 0.051 for 974 reflections with *I* ≥ 3σ(*I*). X-ray analysis indicates that the two methoxycarbonyl groups at C(6) and C(8) are *exo* to the *cis* ring junction and

0108-2701/87/050964-04\$01.50

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*anti* to the dioxolane ring. Both the dioxolane and tetrahydrofuran rings have half-chair conformations with puckering constants  $\Delta = 3.9$ ,  $\varphi_m = -28.6^\circ$  (dioxolane),  $\Delta = 2.4$ ,  $\varphi_m = -32.2^\circ$  (furan). Torsion angles  $O(2)-C(1)-C(5)-C(6) = -124.4$  (3) and  $C(8)-C(1)-C(5)-O(4) = 105.6$  (3) $^\circ$  define the average fold of the molecule as *ca*  $115^\circ$ .

**Introduction.** The ability of enzymes to discriminate between enantiotopic groups of symmetrical substrates such as *meso* compounds is being exploited to an ever increasing extent in asymmetric syntheses (Whitesides & Wong, 1985; Jones, 1985). We are interested in identifying new, stereospecific, enzyme-catalysed transformations of various *meso* compounds into synthetically useful chiral compounds (Lok, Jakovac & Jones, 1985; Jones, Hinks & Hultin, 1985). In this connection the title compound (1) was prepared as a representative substrate for the enzyme-catalysed preparation of chiral synthons of value as precursors to the ribofuranosyl moieties of several C-nucleoside antibiotics (Buchanan, 1983). We report here the X-ray crystallographic confirmation of the *anti* relationship of the dioxolane ring and the methoxycarbonyl groups in (1). Details of the enzyme-catalysed hydrolysis of (1) will be reported in due course.



**Experimental.** Furan-2,5-dicarboxylic acid, prepared from mucic acid in refluxing HBr, was reduced under Birch conditions to give exclusively *cis*-dihydrofuran-2,5-dicarboxylic acid. Fischer esterification, followed by oxidation of the double bond with  $OsO_4$  and *N*-methylmorpholine oxide (NMO) afforded a vicinal diol which was protected as the acetonide (1). Only a single isomer of (1) was isolated. Recrystallization from 6:4 methanol:water solution gave colorless thin elongated plates. Long thin plate of semi-dimensions  $0.015 \times 0.090 \times 0.200$  mm in the directions  $[10\bar{1}]$ ,  $[101]$  and  $[010]$  respectively used throughout. All work on Enraf-Nonius CAD-4 diffractometer using  $MoK\alpha$  radiation. Unit-cell dimensions by least-squares fit of diffracting positions of 25 reflections ( $4.6 < \theta < 16.5^\circ$ ). Peak profiles somewhat broad. Intensity data collected using  $\omega-2\theta$  scans over  $\omega$ -scan ranges  $(0.85 + 0.35 \tan \theta)^\circ$ . Scan rates conditional on information collected in prescans (at  $10^\circ \text{ min}^{-1}$ ) selected to give  $I/\sigma(I) \geq 25$  within a max. scan time of 90 s (50 s for final 470 reflections). Three standard reflections monitored every 9000 s of exposure time showed steady losses in intensity (max. 40%) over data collection

Table 1. Final atomic positional parameters ( $\times 10^4$ ) and thermal parameters ( $\times 10^3$ )

	$U_{eq} = \frac{1}{3} \text{trace } U.$			$U_{eq}(\text{\AA}^2)$
	x	y	z	
C(1)	3799 (4)	2197 (7)	2736 (3)	50 (2)
O(2)	3267 (3)	3698 (6)	3125 (2)	73 (1)
C(3)	3281 (4)	3234 (8)	4081 (3)	53 (2)
O(4)	4128 (2)	1938 (5)	4384 (2)	63.0 (14)
C(5)	4291 (4)	854 (7)	3581 (3)	54 (2)
C(6)	5388 (4)	871 (7)	3596 (3)	52 (2)
O(7)	5554 (2)	2733 (4)	3132 (2)	53.3 (12)
C(8)	4674 (3)	3175 (7)	2427 (3)	47 (2)
C(9)	4800 (5)	2559 (8)	1458 (4)	57 (2)
O(10)	5548 (3)	1986 (7)	1272 (3)	108 (2)
O(11)	3968 (3)	2840 (6)	816 (2)	75 (2)
C(12)	3996 (5)	2528 (10)	-164 (3)	93 (3)
C(13)	5677 (4)	-919 (8)	3047 (4)	54 (2)
O(14)	5108 (3)	-1812 (6)	2434 (3)	98 (2)
O(15)	6642 (3)	-1299 (5)	3292 (2)	61.6 (14)
C(16)	7017 (4)	-2921 (8)	2786 (4)	71 (2)
C(17)	2337 (4)	2169 (9)	4151 (4)	82 (3)
C(18)	3464 (4)	5177 (9)	4649 (4)	79 (2)

period. Backgrounds by extending scan by 25% on either side of peak measured for half the time taken to collect the peak. 3398 reflections in quadrants *h, k, ±l* with  $2\theta \leq 55^\circ$  measured. Lorentz, polarization and corrections for crystal decay [max. rescale factor (on  $F$ ) = 1.88] applied to all reflections. Rejection of 874 systematically absent or zero  $F_{obs}$  data and averaging of 79 symmetry-equivalent reflections ( $R_{int} = 0.026$ ) gave a data set of 2332 reflections. Structure solution: direct methods (*SHELX*; Sheldrick, 1976), least squares, Fourier and  $\Delta F$  Fourier synthesis. Hydrogen atoms located in  $\Delta F$  maps were later placed in calculated positions with a common thermal parameter ( $U = 0.115 \text{ \AA}^2$ ). Full-matrix least-squares refinement (C and O anisotropic) minimizing  $\sum w\Delta F^2$  converged (max.  $\Delta/\sigma = 0.67$ ) to final agreement indices  $R = 0.0513$  ( $wR = 0.0506$ ) for 974 reflections with  $I \geq 3\sigma(I)$ . Weights given by  $w = [\sigma^2(F) + 0.00026F^2]^{-1}$ . Most significant feature in final difference Fourier map was a peak of height  $0.23 \text{ e \AA}^{-3}$  near ( $0.4 \text{ \AA}$ ) H61. Programs: Enraf-Nonius *SDP* package (Frenz, 1980) on a PDP 11/23 computer and *SHELX* on a Gould 9705 computer. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974) were stored in the programs. The final atomic positional and thermal parameters are given in Table 1.\*

**Discussion.** The molecular structure found (Fig. 1) establishes that the methoxycarbonyl groups at C(6) and C(8) are *exo* to the *cis* ring junction and

\* Lists of structure-factor amplitudes, H-atom parameters, torsion angles and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43651 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å), bond angles (°) and selected torsion angles (°)

C(1)–O(2)	1.415 (5)	C(6)–C(13)	1.518 (6)
C(1)–C(5)	1.536 (6)	O(7)–C(8)	1.426 (5)
C(1)–C(8)	1.515 (6)	C(8)–C(9)	1.509 (6)
O(2)–C(3)	1.416 (5)	C(9)–O(10)	1.179 (6)
C(3)–O(4)	1.426 (5)	C(9)–O(11)	1.314 (6)
C(3)–C(17)	1.494 (6)	O(11)–C(12)	1.445 (5)
C(3)–C(18)	1.505 (7)	C(13)–O(14)	1.196 (6)
O(4)–C(5)	1.424 (5)	C(13)–O(15)	1.317 (5)
C(5)–C(6)	1.501 (6)	O(15)–C(16)	1.448 (5)
C(6)–O(7)	1.434 (5)		
O(2)–C(1)–C(5)	104.6 (3)	C(6)–O(7)–C(8)	108.1 (3)
O(2)–C(1)–C(8)	109.8 (4)	O(7)–C(8)–C(1)	107.6 (3)
C(5)–C(1)–C(8)	104.0 (4)	O(7)–C(8)–C(9)	110.9 (4)
C(1)–O(2)–C(3)	110.4 (3)	C(1)–C(8)–C(9)	115.3 (4)
O(2)–C(3)–O(4)	105.1 (4)	C(8)–C(9)–O(10)	125.9 (5)
O(2)–C(3)–C(17)	110.2 (4)	C(8)–C(9)–O(11)	111.0 (5)
O(2)–C(3)–C(18)	108.6 (4)	O(10)–C(9)–O(11)	123.0 (5)
O(4)–C(3)–C(17)	111.1 (4)	C(9)–O(11)–C(12)	117.8 (4)
O(4)–C(3)–C(18)	108.0 (4)	C(6)–C(13)–O(14)	124.3 (5)
C(17)–C(3)–C(18)	113.4 (5)	C(6)–C(13)–O(15)	111.7 (5)
C(3)–O(4)–C(5)	108.1 (3)	O(14)–C(13)–O(15)	123.9 (5)
O(4)–C(5)–C(1)	104.3 (4)	C(13)–O(15)–C(16)	116.9 (4)
O(4)–C(5)–C(6)	109.0 (4)		
C(1)–C(5)–C(6)	105.5 (4)		
C(5)–C(6)–O(7)	105.3 (4)		
C(5)–C(6)–C(13)	111.4 (4)		
O(7)–C(6)–C(13)	108.7 (4)		
C(5)–C(1)–O(2)–C(3)	–7.8 (4)	C(8)–C(1)–C(5)–C(6)	–9.2 (4)
C(1)–O(2)–C(3)–O(4)	22.3 (4)	C(1)–C(5)–C(6)–O(7)	24.9 (4)
O(2)–C(3)–O(4)–C(5)	–28.6 (3)	C(5)–C(6)–O(7)–C(8)	–32.2 (3)
C(3)–O(4)–C(5)–C(1)	23.5 (4)	C(6)–O(7)–C(8)–C(1)	26.4 (4)
O(4)–C(5)–C(1)–O(2)	–9.6 (3)	O(7)–C(8)–C(1)–C(5)	–9.8 (4)

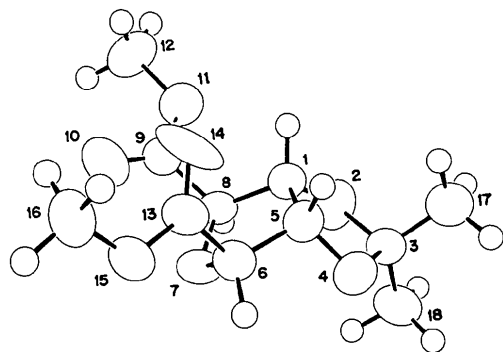


Fig. 1. ORTEP (Johnson, 1965) view of the molecule. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are drawn with uniform isotropic thermal parameters.

*anti* to the dioxolane ring  $\{\tau[\text{O}(2)\text{--C}(1)\text{--C}(8)\text{--C}(9)] = -134.0 (4)$ ;  $\tau[\text{O}(4)\text{--C}(5)\text{--C}(6)\text{--C}(13)] = 155.7 (3)^\circ\}$ . Bond lengths and bond angles in the molecule are given in Table 2. The conformations of the tetrahydrofuran and dioxolane rings are both slightly flattened half-chairs with puckering constants (Altona, Geise & Romers, 1968)  $\Delta = 3.9$ ,  $\varphi_m = -28.6^\circ$  (dioxolane) and  $\Delta = 2.4$ ,  $\varphi_m = -32.2^\circ$  (furan). In the furan ring C(5) is  $-0.395 (4)$  Å and C(8) is  $0.381 (4)$  Å out of the C(1)–C(6)–O(7) plane while in the dioxolane ring O(2) is  $-0.309 (4)$  Å and C(5) is  $0.363 (5)$  Å out of the C(1)–C(3)–O(4) plane. The conformation observed for the dioxolane ring is consistent with the results of a recent molecular-mechanics calculation on 2,2-dimethyl-1,3-dioxolane (Shen, Mathers, Raeker & Hilderbrandt, 1986) which indicated that a twist (half-chair) conformation with puckering constants  $\Delta = 3.3$ ,  $\varphi_m = -38.7^\circ$  is slightly lower in energy than a corresponding envelope conformation. The COC and OCO bond angles used in the calculations do, however, differ by up to  $4^\circ$  from those observed in the present compound.

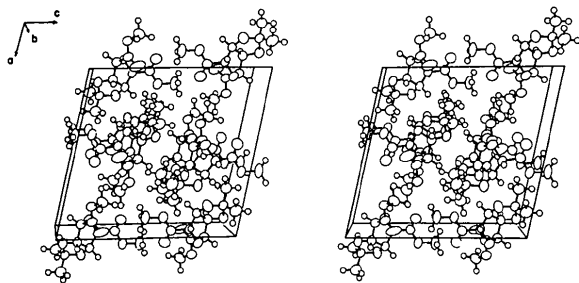
Averaging the absolute values of the torsion angles  $\tau[\text{O}(2)\text{--C}(1)\text{--C}(5)\text{--C}(6)] = -124.4 (3)$  and  $\tau[\text{C}(8)\text{--C}(1)\text{--C}(5)\text{--O}(4)] = 105.6 (3)^\circ$  defines the fold of the molecule as  $115.0^\circ$ . Atoms C(6) and C(8) are  $0.067 (5)$  and  $0.148 (5)$  Å respectively out of the mean planes through the methoxycarbonyl groups. Torsion angles  $\tau[\text{C}(1)\text{--C}(8)\text{--C}(9)\text{--O}(10)] = -130.1 (5)$  and  $\tau[\text{C}(5)\text{--C}(6)\text{--C}(13)\text{--O}(14)] = 23.4 (6)^\circ$  indicate that the planes of the methoxycarbonyl groups are rotated by *ca*  $153^\circ$  with respect to one another.

The crystal packing is shown in Fig. 2. Intermolecular contacts are generally weak, the shortest being  $\text{O}(10)\cdots\text{H}(16A)$  ( $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ ) =  $2.25$  Å [ $\text{C}(9)\text{--O}(10)\cdots\text{H}(16A) = 136.3$ ;  $\text{C}(16)\text{--H}(16A)\cdots\text{O}(10) = 169.3^\circ$ ] and  $\text{H}(12A)\cdots\text{H}(16B) = 2.06$  Å.

We thank the Natural Sciences and Engineering Research Council of Canada for support of this work.

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Fig. 2. Stereoscopic view down *b* of the crystal packing.

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*Acta Cryst.* (1987). **C43**, 967–968

## Structure of 2,4-Dibromo-10 $\beta$ ,17 $\beta$ -dihydroxy-1,4-estradien-3-one

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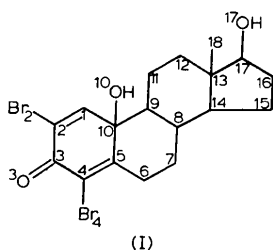
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(Received 20 June 1986; accepted 12 December 1986)

**Abstract.** C<sub>18</sub>H<sub>22</sub>Br<sub>2</sub>O<sub>3</sub>,  $M_r = 446.19$ , tetragonal,  $P4_1$ ,  $a = 9.4634(3)$ ,  $c = 20.0447(15)$  Å,  $V = 1795.1(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.650$  Mg m<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 5.875$  mm<sup>-1</sup>,  $F(000) = 896$ , room temperature, final  $R = 4.1\%$  for 1826 reflections. The hydroxyl group at C(10) exists in a  $\beta$  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.



**Experimental.** Recrystallization from methanol, single crystal  $0.30 \times 0.30 \times 0.68$  mm. The unit-cell parameters were refined from accurately measured  $2\theta$  values of 25 reflections from the range  $71 < 2\theta < 84^\circ$ . Intensities of 2343 unique reflections having  $\theta < 77^\circ$  ( $0 \leq h \leq 11$ ,  $0 \leq k \leq 11$ ,  $-25 \leq l \leq 1$ ) 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  $\leq 5\%$  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  $I > 2.0\sigma(I)$ . Hydrogens found from  $\Delta F$  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  $R = 4.1\%$ ,  $wR = 5.4\%$ ,  $S = 2.523$  for observed reflections,  $w = 1/\sigma_F^2$ ,  $(\Delta/\sigma)_{\max} = 0.38$ . Final difference maps showed strongest peak (trough) of  $+0.60$  ( $-0.70$ ) e Å<sup>-3</sup>. 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.