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Structure of Ethyl 4-(α-D-Erythrofuranosyl)-1,2-dimethyl-3-pyrrolecarboxylate, $C_{13}H_{19}NO_5$

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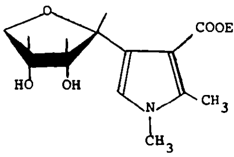
Abstract. $M_r = 269·3$, orthorhombic, $P2_12_12_1$, $a = 11·401\ (2)$, $b = 24·336\ (4)$, $c = 4·691\ (3)$ Å, $V = 1301·5\ (9)$ Å^3, $Z = 4$, $D_x = 1·37$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0·7107$ Å) = 0·099 mm^{-1}, $F(000) = 576$, $T = 300$ K, final $R = 0·060$ for 1170 observed independent reflexions. The sugar ring is puckered in the $^3T_2$ mode conformation and the dihedral angle it forms with the pyrrole ring is 39·7 (3)°. No evidence of hydrogen bonding has been detected.

Introduction. The structure determination of the title compound was undertaken as part of a wider research project involving heterocyclic *C*-nucleosides, whose principal aim is to establish the conformational details of the molecular structure in the solid state. The title compound has been prepared by forming the anhydride of ethyl 1,2-dimethyl-4-(D-*arabino*-1,2,3,4-tetrahydroxybutyl)-3-pyrrolecarboxylate in acid medium, followed by chromatographic isolation (Fernández-Bolaños, Fuentes & Robina, 1982). Its chemical nature was established from elemental analysis and spectroscopic data (UV, IR and NMR), and the X-ray analysis was carried out to define the structural details.



Experimental. Single crystals in the form of colourless prisms elongated along **c** were prepared in the Organic Chemistry Department of this University and kindly supplied by Professor J. Fernández-Bolaños. Unit-cell parameters calculated by least squares from 25 reflexions, Enraf–Nonius CAD-4 diffractometer, intensity data up to $2\theta = 60°$ ($h < 17$, $k < 35$, $l < 7$), ω–2θ scan mode; three reflexions monitored during data collection, variation in intensity less than 2% of its mean value; intensities of 2259 independent reflexions measured, 1089 considered unobserved [$I < 2\sigma(I)$], Lorentz and polarization corrections, no corrections for absorption ($\mu R < 0·1$) or extinction; direct methods with *MULTAN* 80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and 226 reflexions with $E > 1·56$; an E map computed for the best set of phases showed the positions of all the non-hydrogen atoms; after full-matrix least-squares refinement based on F with anisotropic temperature factors a difference Fourier synthesis (calculated up to $\sin\theta/\lambda = 0·6$ Å^{-1}) revealed the 19 H atoms; an isotropic temperature factor was assigned to each H atom equal to that of the atom bonded to it; further least-squares refinement including the positional parameters of the H atoms reduced wR to 0·062,* weighting scheme based on a statistical count criterion; mean shift in the last cycle of refinement $0·2\sigma$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); XRAY system (Stewart, Kundell & Baldwin, 1970).

Discussion. Fractional atomic coordinates are given in Table 1. Bond lengths and angles involving non-hydrogen atoms with their estimated standard deviations are given in Fig. 1. C–H bond distances range from 0·92 to 1·16 Å with an average value of 1·05 (7) Å. The average C–O bond length is 0·83 (8) Å.

Sugar ring. Bond lengths and angles in the furanosyl ring are similar to those found in analogous compounds. However, the endocyclic C—O bond lengths C(5)–O(1) = 1·447 (7) and C(6)–O(1) = 1·418 (8) Å are asymmetric and this asymmetry had been found previously for β anomers. Average values for C–C–C, C–C–O and C–O–C endocyclic angles of 100·6 (5), 105·9 (5) and 109·5 (5)° agree with the mean values reported elsewhere (Conde, López-Castro & Márquez, 1978). The sugar ring is not planar as expected. Deviations from the least-squares plane through the five atoms of the ring are shown in Table 2 and the sugar-ring puckering is C(8)-*endo*, C(7)-*exo*. In terms of ring-puckering coordinates (Cremer & Pople, 1975) the amplitude phase magnitudes are $q = 0·412\ (8)$ Å

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38158 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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and $\varphi = 276 \cdot 3\ (6)^\circ$ for the sequence O(1)C(6)C(7)-C(8)C(5) and the resulting conformation corresponds to the $^3T_2$ mode.

Table 1. *Atomic fractional coordinates* (×10^4, *for* H ×10^3) *and equivalent isotropic temperature factors*

$$B_{\rm eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$ (Å^2)
N	−1183 (5)	2150 (2)	8076 (13)	3·2 (2)
C(1)	−1907 (6)	1830 (3)	6510 (16)	2·8 (2)
C(2)	−1215 (6)	1479 (2)	4877 (14)	2·4 (2)
C(3)	−18 (6)	1606 (3)	5531 (15)	2·5 (2)
C(4)	−28 (6)	2014 (3)	7514 (17)	2·9 (2)
C(5)	1063 (5)	1352 (2)	4324 (14)	2·2 (2)
C(6)	3018 (6)	1292 (3)	5808 (19)	3·2 (2)
C(7)	2645 (5)	737 (3)	4644 (14)	2·3 (2)
C(8)	1313 (5)	756 (3)	5146 (13)	2·1 (2)
C(9)	−1516 (8)	2581 (3)	10062 (20)	4·1 (2)
C(10)	−3213 (6)	1915 (3)	6722 (21)	4·1 (2)
C(11)	−1584 (6)	1070 (3)	2839 (16)	2·8 (2)
C(12)	−3176 (7)	591 (3)	682 (21)	4·3 (2)
C(13)	−4499 (8)	606 (4)	926 (30)	6·4 (3)
O(1)	2071 (4)	1658 (2)	5316 (12)	3·0 (1)
O(2)	−2753 (4)	1002 (2)	2725 (13)	3·9 (2)
O(3)	−934 (4)	798 (2)	1369 (11)	3·5 (2)
O(4)	1134 (4)	660 (2)	8118 (9)	2·8 (1)
O(5)	3227 (4)	308 (2)	6043 (11)	2·8 (1)
H(C4)	76 (7)	228 (3)	816 (22)	
H(C5)	108 (7)	140 (3)	194 (19)	
H1(C6)	329 (8)	125 (3)	803 (22)	
H2(C6)	374 (8)	144 (3)	500 (22)	
H(C7)	274 (7)	72 (3)	258 (19)	
H(C8)	95 (7)	41 (3)	411 (20)	
H1(C9)	−88 (8)	280 (4)	1100 (25)	
H2(C9)	−196 (8)	286 (4)	923 (25)	
H3(C9)	−224 (9)	243 (4)	1165 (24)	
H1(C10)	−342 (8)	222 (4)	515 (25)	
H2(C10)	−363 (9)	165 (4)	532 (25)	
H3(C10)	−347 (9)	178 (4)	848 (25)	
H1(C12)	−307 (8)	74 (4)	−157 (25)	
H2(C12)	−289 (8)	19 (4)	115 (30)	
H1(C13)	−481 (11)	46 (5)	282 (30)	
H2(C13)	−466 (10)	24 (4)	−34 (29)	
H3(C13)	−478 (9)	102 (4)	45 (29)	
H(O4)	37 (7)	73 (3)	845 (21)	
H(O5)	326 (8)	5 (4)	508 (23)	

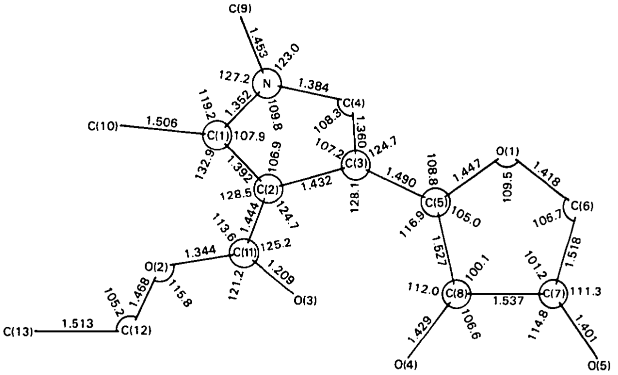

Fig. 1. Bond lengths (Å) and angles (°) in the molecule. (Standard deviations are in the ranges 0·007–0·011 Å and 0·5–0·6°, respectively.)

Pyrrole ring. Bond lengths and angles agree quite well with the values reported for other compounds (Conde, López-Castro & Márquez, 1979). The lengthening of the formal double bonds C(1)–C(2) and C(3)–C(4) and the shortening of the other three bonds of the pyrrole ring indicate considerable delocalization of the double-bond π electrons. The marked asymmetry of the endocyclic C(1)–N and C(4)–N may be explained in terms of contributions from mesomeric forms (Sheldrick, Becker & Engel, 1978). As expected, the pyrrole ring is planar; ring atoms do not deviate significantly (Table 2) from their least-squares plane.

Molecular conformation and packing. The ethoxycarbonyl group is nearly coplanar with the pyrrole ring. The dihedral angle between the least-squares planes of both groups is 4·3 (7)°.

The relative orientation of the pyrrole ring with respect to the furanose ring can be described by the torsion angle C(2)–C(3)–C(5)–O(1) = 172·4 (6)° (Table 3). The dihedral angle between both rings is 39·7 (3) °.

A view of the unit-cell contents down **c** is shown in Fig. 2. Packing of the molecules in the crystal is due to van der Waals interactions only. No evidence for hydrogen bonds has been detected and there is no intermolecular contact significantly shorter than the sum of the van der Waals radii.

Table 2. *Least-squares planes through molecular fragments*

(*a*) Equations of the planes

(I) Furan ring	$0 \cdot 1409x + 0 \cdot 0636y - 0 \cdot 9880z = -1 \cdot 8230$
(II) Pyrrole ring	$0 \cdot 0171x + 0 \cdot 6783y - 0 \cdot 7346z = +0 \cdot 7401$
(III) Ethoxycarbonyl group	$0 \cdot 0476x - 0 \cdot 7016y + 0 \cdot 7110z = -0 \cdot 9575$

(*b*) Atomic deviations (Å × 10^3) from the planes

(I)		(II)		(III)	
C(5)	199 (7)	N	3 (6)	C(13)	13 (13)
O(1)	−51 (6)	C(1)	0 (7)	C(12)	−4 (9)
C(6)	−184 (9)	C(2)	−2 (6)	O(2)	−5 (6)
C(7)	210 (7)	C(3)	5 (7)	C(11)	8 (7)
C(8)	−234 (6)	C(4)	−6 (8)	O(3)	−1 (5)
C(3)*	−495 (7)	C(9)*	23 (9)	C(2)*	8 (6)
O(4)*	−1655 (5)	C(10)*	42 (9)		
O(5)*	−412 (6)	C(11)*	16 (7)		
		C(5)*	22 (6)		

* Atoms not included in the calcuiation of the least-squares planes.

Table 3. *Selected torsion angles* (°)

N–C(1)–C(2)–C(3)	−0·2 (8)	C(2)–C(11)–O(2)–C(12)	179·9 (6)
C(1)–C(2)–C(3)–C(4)	0·7 (8)	C(11)–O(2)–C(12)–C(13)	−178·7 (7)
C(2)–C(3)–C(4)–N	−1·0 (8)	C(2)–C(3)–C(5)–O(1)	172·4 (6)
C(3)–C(4)–N–C(1)	0·9 (8)	C(4)–C(3)–C(5)–C(8)	111·1 (7)
C(4)–N–C(1)–C(2)	−0·4 (8)	C(3)–C(5)–C(8)–C(7)	−157·0 (5)
C(9)–N–C(4)–C(3)	−178·7 (6)	C(5)–O(1)–C(6)–C(7)	8·8 (7)
C(10)–C(1)–N–C(9)	1·0 (11)	O(1)–C(6)–C(7)–C(8)	−31·4 (6)
C(10)–C(1)–C(2)–C(3)	177·6 (7)	C(6)–C(7)–C(8)–O(5)	40·4 (6)
N–C(1)–C(2)–C(11)	−178·9 (6)	C(7)–C(8)–C(5)–O(1)	−36·4 (6)
N–C(4)–C(3)–C(5)	178·9 (6)	C(8)–C(5)–O(1)–C(6)	18·0 (6)
C(11)–C(2)–C(3)–C(5)	−0·5 (11)	O(1)–C(6)–C(7)–O(5)	−153·8 (5)
C(10)–C(1)–C(2)–C(11)	−1·1 (12)	O(1)–C(5)–C(8)–O(4)	76·2 (6)
C(1)–C(2)–C(11)–O(3)	175·7 (6)	O(5)–C(7)–C(8)–O(4)	43·5 (7)
C(3)–C(2)–C(11)–O(2)	176·1 (6)		

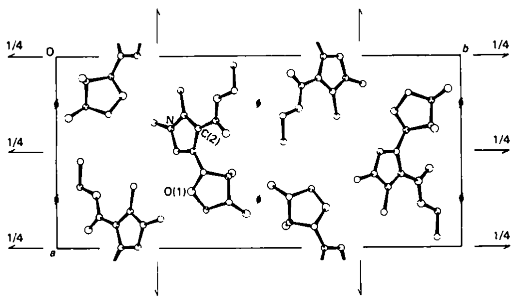

Fig. 2. A view along [001] of the unit-cell contents.

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Structure of 4-(β-D-Erythrofuranosyl)-3-methyl-1-(*p*-tolyl)-4-imidazoline-2-thione Monohydrate, $C_{15}H_{18}N_2O_3S.H_2O$

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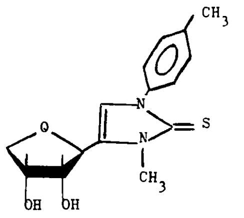
Abstract. $M_r = 324{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 32{\cdot}150\ (5)$, $b = 10{\cdot}215\ (1)$, $c = 4{\cdot}805\ (1)$ Å, $V = 1578{\cdot}0\ (4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}36$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 1{\cdot}953$ mm^{-1}, $T = 300$ K, final $R = 0{\cdot}050$ for 1361 observed $[I > 2\sigma(I)]$ independent reflexions. The sugar ring adopts a conformation intermediate between envelope ^2E and twist ^2_1T forms. The orientation of the imidazoline ring with respect to the furanose is *anti*; the glycosidic angle is 24·6 (7)°. The crystal packing is due to hydrogen bonds involving the hydration water molecules.

Introduction. Heterocyclic *C*-nucleosides are interesting because of their structural analogies with natural *C*-nucleosides and because of their antiviral activity (Hanessian & Pernet, 1976).

Potential anticancer and radioprotective characteristics were reported (Weitzel, Schneider, Guglielmi, Sander, Durst & Hirschmann, 1966) for imidazole *C*-nucleosides.

The crystal structure of the title compound has been determined as part of a systematic structural investigation of imidazole *C*-nucleosides synthesized (Fernández-Bolaños, Fuentes-Mota, Barragán Peréz & Pradera de Fuentes, 1978) in the Organic Chemistry Department of this University.



(I)

The title compound (I) was obtained (Fernández-Bolaños, Fuentes-Mota & Fernández-Bolaños Guzmán, 1982) by the catalyzed formation of the anhydride of 3-methyl-4-(D-*arabino*-1,2,3,4-tetrahydroxybutyl)-1-(*p*-tolyl)-4-imidazoline-2-thione and it is the first disubstituted (at both atoms) imidazole *C*-nucleoside.

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