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Structure and Absolute Configuration of 4-(α-D-Erythrofuranosyl)-1,3-dihydro-3-methyl-1-(*p*-tolyl)-2*H*-imidazole-2-thione, $C_{15}H_{18}N_2O_3S$

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Abstract. $M_r = 306.4$, monoclinic, $P2_1$, $a = 14.686$ (6), $b = 5.359$ (4), $c = 9.439$ (3) Å, $\beta = 98.68$ (3)°, $V = 734.4$ (7) Å^3, $Z = 2$, $D_x = 1.38$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.22$ mm^{-1}, $F(000) = 324$, $T = 300$ K, final $R = 0.042$ ($wR = 0.037$) for 1987 observed independent reflections. The sugar ring has a conformation intermediate between $^3T_2$ and ^3E. The configuration of the imidazole ring with respect to the furanose ring is *anti*, the glycosidic angle being -9.3 (4)°. The crystal packing is governed by hydrogen bonds involving OH groups and S atoms, forming infinite chains along [001].

Introduction. The title compound (I) was obtained (Fernández-Bolaños, Fuentes-Mota & Fernández-Bolaños Guzmán, 1983) by the catalysed formation of the anhydride of 1,3-dihydro-3-methyl-4-(D-*arabino*-1,2,3,4-tetrahydroxybutyl)-1-(*p*-tolyl)-2*H*-imidazole-2-thione. By the same process the *β* anomer was also obtained, and its structure reported by Criado, Conde & Márquez (1983). The structural study of both anomers forms part of a systematic research project dealing with D-erythrofuranosyldihydroimidazole-2-thione compounds (Conde, López-Castro & Márquez, 1978) prepared in the Organic Chemistry Department of this University.

(I)
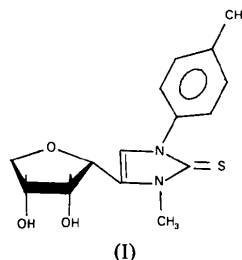
A conformational study of sugar rings for both compounds has been performed by means of the ^{1}H NMR technique in solution, and the results (Fernández-Bolaños Guzmán, 1984) agree with X-ray data in the solid state.

Experimental. Needle-shaped colourless crystals, supplied by Professor Fernández-Bolaños of the Organic Chemistry Department of this University. Weissenberg diagrams showed monoclinic symmetry; space group $P2_1$ from systematic absences. CAD-4 computer-controlled diffractometer, graphite-monochromated radiation. Crystal $0.1 \times 0.2 \times 1.1$ mm. Unit-cell parameters from least-squares fit of θ values of 25 reflections, $6 < \theta < 15°$. 2352 reflections measured with $\theta < 30°$ $(-20 \le h \le 20, \ 0 \le k \le 7, \ 0 \le l \le 13)$. $\omega-2\theta$ scan mode. 1987 reflections with $I > 2\sigma(I)$ considered observed. Two reference reflections controlled periodically, intensity changes less than 3%. Lorentz and polarization corrections. No absorption or extinction effects considered. Weighted tangent-formula refinement (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) of 234 reflections with $E > 1.5$. Full-matrix least-squares refinement of 189 parameters based on F_o with all observed reflections (*CRYLSQ* of *XRAY*70; Stewart, Kundell & Baldwin, 1970). Fourier difference synthesis up to $\sin\theta/\lambda = 0.7$ Å^{-1} gave all H-atom positions; a least-squares refinement in a mixed mode with H atoms, each with an isotropic temperature factor equal to that of the attached skeleton atom, gave $wR = 0.037$ $(R = 0.042)$. Final-cycle parameter shifts less than 0.1σ, average 0.05σ. Final difference Fourier map $-0.21 < \Delta\rho < 0.29$ e Å^{-3}. $S = 2.35$ for 244 parameters. Atomic scattering factors and anomalous-dispersion corrections for S from *International Tables for X-ray Crystallography* (1974). Weighting scheme $1/\sigma^2(I)$ based on counting statistics. The enantiomorphic form was considered and the final $wR = 0.038$ $(R = 0.043)$. The application of the $\mathscr{R}$ test (Hamilton, 1965) indicated that the first form is correct $\{[wR(2)/wR(1)] = 1.027;$ $\mathscr{R}_{1,1744,0.005} = 1.002\}$ and can be retained as the absolute configuration. This form is consistent with the configuration of the sugar used in the synthesis.

Discussion. Final atomic coordinates and equivalent isotropic thermal parameters (Hamilton, 1956) for non-H atoms are given in Table 1.* Bond lengths and angles are shown in Table 2. The C—H distances are 0.84 (4) to 1.10 (4) Å with a mean of 0.97 (3) Å. The average O—H bond length is 0.90 (3) Å.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42175 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Imidazole ring. Bond lengths and angles in the imidazole ring are quite similar to those found in the β anomer (Criado, Conde & Márquez, 1983) and other analogous imidazole-2-thione compounds studied previously (Conde, López-Castro & Márquez, 1978). Partial double-bond character is found for the S—C bond, also present in the above-mentioned compounds, in agreement with canonical resonance forms in the thiourea system.

Table 1. *Positional parameters* $(\times 10^4)$ *and equivalent isotropic thermal parameters* $(\times 10^4)$ *for the non-H atoms, with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2)
S	8330 (1)	5000	−3021 (1)	449 (3)
N(1)	7238 (1)	5112 (5)	−901 (2)	334 (6)
N(2)	8400 (1)	7656 (5)	−545 (2)	316 (7)
O(1)	7426 (1)	9943 (5)	2583 (2)	484 (7)
O(2)	9330 (1)	9447 (4)	5460 (2)	439 (7)
O(3)	9098 (1)	6517 (4)	2964 (2)	567 (8)
C(1)	7984 (2)	5924 (5)	−1486 (3)	308 (8)
C(2)	7199 (2)	6381 (6)	375 (3)	380 (9)
C(3)	7912 (2)	7958 (6)	598 (2)	332 (8)
C(4)	8173 (1)	9794 (6)	1770 (2)	363 (8)
C(5)	7768 (2)	9841 (9)	4068 (3)	560 (11)
C(6)	8794 (2)	10335 (6)	4201 (3)	375 (8)
C(7)	9030 (2)	9128 (6)	2844 (3)	368 (9)
C(8)	6502 (2)	3565 (5)	−1596 (3)	327 (8)
C(9)	6670 (2)	1420 (6)	−2324 (3)	373 (9)
C(10)	5935 (2)	42 (7)	−3006 (3)	432 (9)
C(11)	5030 (2)	774 (6)	−2981 (3)	433 (10)
C(12)	4879 (2)	2915 (7)	−2217 (3)	447 (10)
C(13)	5601 (2)	4303 (6)	−1525 (3)	413 (9)
C(14)	4225 (2)	−681 (7)	−3753 (4)	647 (13)
C(15)	9215 (2)	9062 (6)	−756 (3)	433 (9)

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

S—C(1)	1.681 (3)	C(3)—C(4)	1.487 (4)
N(1)—C(1)	1.370 (3)	C(4)—C(7)	1.534 (3)
N(1)—C(2)	1.391 (3)	C(5)—C(6)	1.515 (4)
N(1)—C(8)	1.439 (3)	C(6)—C(7)	1.522 (4)
N(2)—C(1)	1.364 (3)	C(8)—C(9)	1.380 (4)
N(2)—C(3)	1.391 (3)	C(8)—C(13)	1.392 (4)
N(2)—C(15)	1.453 (4)	C(9)—C(10)	1.384 (4)
O(1)—C(4)	1.433 (3)	C(10)—C(11)	1.390 (4)
O(1)—C(5)	1.418 (3)	C(11)—C(12)	1.391 (5)
O(2)—C(6)	1.406 (3)	C(11)—C(14)	1.508 (4)
O(3)—C(7)	1.406 (4)	C(12)—C(13)	1.377 (4)
C(2)—C(3)	1.337 (4)		

C(2)—N(1)—C(8)	123.4 (2)	O(1)—C(5)—C(6)	106.0 (2)
C(1)—N(1)—C(8)	126.2 (2)	O(2)—C(6)—C(5)	115.7 (2)
C(1)—N(1)—C(2)	109.5 (2)	C(5)—C(6)—C(7)	101.9 (2)
C(3)—N(2)—C(15)	125.2 (2)	O(2)—C(6)—C(7)	113.4 (2)
C(1)—N(2)—C(15)	124.1 (2)	C(4)—C(7)—C(6)	100.9 (2)
C(1)—N(2)—C(3)	110.6 (2)	O(3)—C(7)—C(6)	112.2 (3)
C(4)—O(1)—C(5)	109.9 (2)	O(3)—C(7)—C(4)	109.0 (3)
N(1)—C(1)—N(2)	105.1 (2)	N(1)—C(8)—C(13)	117.9 (3)
S—C(1)—N(2)	126.7 (2)	N(1)—C(8)—C(9)	121.9 (3)
S—C(1)—N(1)	128.2 (2)	C(9)—C(8)—C(13)	120.2 (3)
N(1)—C(2)—C(3)	108.2 (2)	C(8)—C(9)—C(10)	119.4 (3)
N(2)—C(3)—C(2)	106.7 (2)	C(9)—C(10)—C(11)	121.4 (3)
C(2)—C(3)—C(4)	130.0 (3)	C(10)—C(11)—C(14)	121.8 (3)
N(2)—C(3)—C(4)	123.3 (2)	C(10)—C(11)—C(12)	118.0 (3)
O(1)—C(4)—C(3)	107.6 (2)	C(12)—C(11)—C(14)	120.2 (3)
C(3)—C(4)—C(7)	115.5 (3)	C(11)—C(12)—C(13)	121.3 (3)
O(1)—C(4)—C(7)	106.1 (2)	C(8)—C(13)—C(12)	119.5 (3)

$C_{15}H_{18}N_2O_3S$

The ring deviates very slightly from expected planarity [$\sum(\Delta/\sigma)^2 = 11.74$; χ^2 for two degrees of freedom at 95% is 5.99]. The maximum atomic deviation from the least-squares plane is 0.006 (3) Å.

Phenyl ring. The mean value of the C—C bond length in the phenyl group is 1.385 (4) Å and the average C—C—C bond angle is 120.0 (3)°. The observed deviation from planarity [$\sum(\Delta/\sigma)^2 = 36.0$] could not be real. The dihedral angle between the phenyl and imidazole rings is 42.2 (1)°, very close to the 40.7 (2)° found in the β anomer and the same conclusions are derived here: crystal forces contribute significantly to phenyl–imidazole subrotation.

Furanosyl ring. Bond lengths and angles are in agreement with the values corresponding to the β anomer and other similar reported compounds. The typical asymmetry of the endocyclic bonds O(1)—C(4) 1.433 (3) and O(1)—C(5) = 1.418 (3) Å due to anomeric effects is observed. Average values for C—C—C 101.4 (3), C—C—O 106.0 (2) and C—O—C 109.9 (2)° agree with the mean values reported previously (Conde, López-Castro & Márquez, 1978). The furanosyl ring is not planar, and in terms of the ring-puckering coordinates (Cremer & Pople, 1975) the amplitude phase magnitudes are $Q = 0.382$ (4) Å and $\varphi = -86.2$ (6)° for the sequence O(1)—C(4)—C(7)—C(6)—C(5). The conformation is different from that of the β anomer, but the values of the pseudorotational parameters τ_m and P place the conformation in one of the most statistically crowded regions of the conformational wheel (Pullman, 1976), whereas the β anomer lies in another crowded region. The asymmetry parameters $\Delta C_2[O(1)] = 0.0155$ (24) and $\Delta C_s[C(6)] = 0.0738$ (33) (Nardelli, 1983) show a conformation intermediate between $^3T_2$ and ^3E.

Molecular conformation. The orientation of imidazole with respect to furanose is *anti*. The glycosidic torsion angle O(1)—C(4)—C(3)—C(2) (Sundaralingam, 1969) is −9.3 (4)°. The β anomer has a value of 24.6 (7)°, and is also *anti*; no correlation has been found between sugar conformation and glycosidic angles. Both *anti* and *syn* conformations have been found in previous structural analysis of imidazole C-nucleosides.

Crystal packing. Fig. 1 shows the contents of the unit cell viewed along **b**. Packing is due to hydrogen bonds. Each molecule is linked by a hydrogen bond to another molecule related to the former by a lattice translation along **c**, resulting in a pattern of infinite chains parallel to **c**: O(2)—H(O2)···S(x, y, $1 + z$) with H(O2)···S 2.35 (3), O(2)—H(O2) 0.90 (3), O(2)···S 3.244 (3) Å, O(2)—H(O2)···S 172 (3)°. On the other hand, molecules related by a twofold screw axis are linked by O(3)—H(O3)···O(2)($2 - x$, $y - \frac{1}{2}$, $1 - z$) to form helical chains parallel to [010]: O(3)—H(O3) 0.91 (3), H(O3)···O(2) 1.91 (3), O(3)···O(2) 2.781 (2) Å, O(3)—H(O3)···O(2) 160 (3)°. No other intermolecular contacts shorter than the sum of the van der Waals radii have been detected.
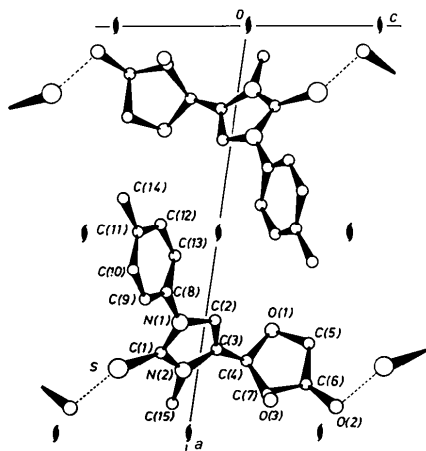
Fig. 1. The unit cell viewed along **b**. Broken lines are hydrogen bonds.

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