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Note

Crystal and molecular structure of 5-(α-D-erythrofuranosyl)-3-methyl-2(3*H*)-thiazole-2-thione

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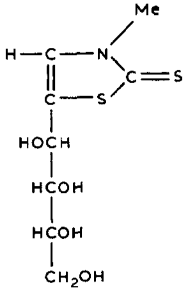
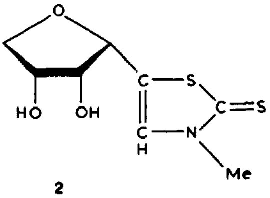
The synthesis of *C*-nucleosides[1] has received attention due to their antitumour and antiviral activities[2]. However, little effort has been devoted to the synthesis of *C*-nucleoside analogues of 2(3*H*)-thiazole-2-thiones. The synthesis of 5-(α- and β-D-erythrofuranosyl)-3-methyl-2(3*H*)-thiazole-2-thiones (**2**) has been achieved[3] by acid-catalysed dehydration of 3-methyl-5-(D-*arabino*-tetritol-1-yl)-2-(3*H*)-thiazole-2-thiones[3,4] (**1**).



1



2

The positional and isotropic thermal parameters for the non-hydrogen atoms of **2** are given in Table I, and the bond lengths and angles together with their estimated standard deviations are given in Table II. The C–H distances range from 0.984 to 1.046 Å with an average value of 1.010 Å. The average O–H distance is 1.013 Å.

The thiazole ring is practically planar [maximum deviation from the least-squares plane, 0.015(16) Å]; the substituents S-2 and C-8 also lie in this plane [at 0.049(7) and −0.032(22) Å, respectively, from the mean square plane], whereas the other substituent, C-4, shows a small but significant out-of-plane deviation of 0.168(16) Å.

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TABLE I

NON-HYDROGEN ATOMIC CO-ORDINATES (× 10^3) FOR **2** (E.S.D. VALUES IN PARENTHESES) AND THERMAL PARAMETERS (× 10^2)

Atom	x/a	y/b	z/c	U_{eq}
S-1	828(1)	200(0)	715(1)	4.6(2)
S-2	994(1)	357(1)	983(1)	6.9(3)
O-1	1019(1)	99(1)	433(1)	4.7(6)
C-3	1019(2)	70(1)	670(1)	4.0(8)
C-1	1031(3)	236(1)	869(1)	4.5(9)
C-8	430(3)	147(2)	1001(1)	7.4(9)
N-1	226(2)	147(1)	880(1)	4.1(7)
C-4	980(2)	−3(1)	533(1)	3.6(8)
C-7	841(2)	86(1)	310(1)	3.6(7)
C-2	1217(2)	57(1)	768(1)	4.6(9)
C-5	720(2)	−64(1)	475(1)	4.7(9)
C-6	609(2)	32(1)	352(1)	3.3(7)
O-3	485(1)	146(1)	393(1)	5.8(7)
O-2	566(1)	−73(1)	568(1)	4.6(6)

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

TABLE II

BOND LENGTHS (Å) AND ANGLES (DEGREES) FOR **2**[a]

Bond lengths			
S-1–C-3	1.748	C-8–N-1	1.468
S-1–C-1	1.728	N-1–C-2	1.386
S-2–C-1	1.654	C-4–C-5	1.559
O-1–C-4	1.440	C-7–C-6	1.530
O-1–C-7	1.401	C-5–C-6	1.546
C-3–C-4	1.504	C-5–O-2	1.400
C-3–C-2	1.313	C-6–O-3	1.387
C-1–N-1	1.365		
Bond angles			
C-3–S-1–C-1	92.6	C-3–C-4–C-5	116.7
C-4–O-1–C-7	110.9	O-1–C-4–C-5	105.2
S-1–C-3–C-2	109.7	O-1–C-7–C-6	105.8
S-1–C-3–C-4	125.6	C-3–C-2–N-1	114.5
C-4–C-3–C-2	124.1	C-4–C-5–O-2	115.6
S-1–C-1–S-2	125.8	C-4–C-5–C-6	104.4
S-2–C-1–N-1	126.3	C-6–C-5–O-2	111.1
S-1–C-1–N-1	107.7	C-1–N-1–C-8	121.8
C-8–N-1–C-2	122.9	C-7–C-6–C-5	101.3
C-1–N-1–C-2	115.2	C-5–C-6–O-3	111.7
O-1–C-4–C-3	107.4	C-7–C-6–O-3	109.1

[a] Mean e.s.d.'s 0.019 Å and 1.2°.

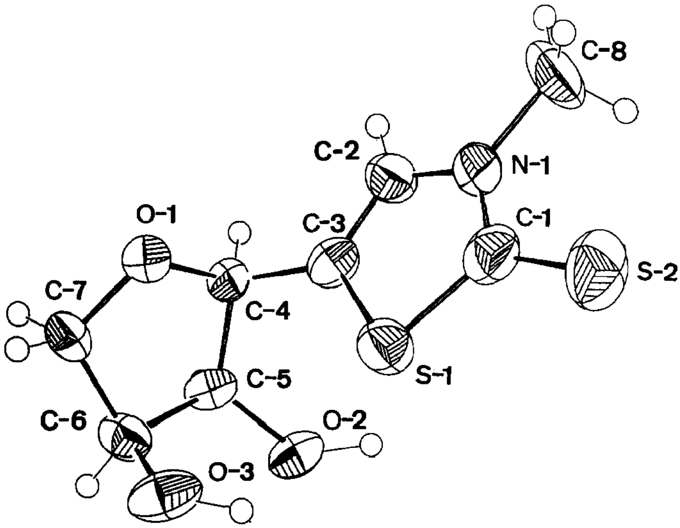

Fig. 1. ORTEP[13] view of **2** along *ac*, showing the atomic numbering. Thermal ellipsoids enclose 50% probability.

The data in Table II agree quite well with those reported for analogous thiazoline-2-thiones[8,10]. The exocyclic C–S bond-length of 1.654(17) Å agrees with the distance found for this bond in the resonance forms of the thiourea system[11]. The hybridisation nature of C-1, N-1, C-2, and C-3 are all sp^2. The endocyclic C-1–S-1–C-3 angle is 92.6(8)°.

The furanose ring is not planar as expected. In terms of ring-puckering coordinates[12], the amplitude phase magnitudes are $q = 0.33(1)$ Å and $\phi = -55(2)°$ for the sequence O-1–C-4–C-5–C-6–C-7 and the resulting conformation is twist ${}^3_4T$, where C-6 and C-7 deviate by −0.27(1) and +0.28(1) Å, respectively, from the O-1–C-4–C-5 plane. The dihedral angle between the best plane of the furanose and thiazole rings is 93.8(5)°. The torsion angles S-1–C-3–C-4–O-1 and C-2–C-3–C-4–C-5 are 68(1) and 138(1)°, respectively. O-2, O-3, and C-3 are on the same side of the furanose ring, which confirms the α configuration for **2**; O-3 is axial and O-2 is quasi-equatorial (Fig. 1).

The endocyclic C–O bond-lengths [C-7–O-1 = 1.401(15) and O-1–C-4 = 1.440(19) Å] are asymmetric, reflecting the anomeric effect, a normal feature of this group. The average values of the C–C–C, C–C–O and C–O–C endocyclic angles are 102.9, 105.6, and 111.0°, respectively. The packing of the molecules in the crystal is governed by van der Waals interactions and two possible hydrogen bonds: O-2 · · · O-3 $(-x + 1, y - 1/2, -z + 1) = 2.707(16)$, and O-3 · · · O-1 $(x - 1, y, z) = 2.754(15)$ Å.

EXPERIMENTAL

Single crystals of **2** {m.p. 233°, $[\alpha]_D^{22}$ +58° (*c* 1, pyridine)} were in the form of clear maroon prisms. The chosen crystal had an approximate size of 0.50 × 0.15 × 0.17 mm and belonged to the monoclinic system with systematic absences consistent with $P2_1$. The lattice parameters, refined using 25 reflections within the range $6 \leq \theta \leq 12°$, were a = 5.586(3), b = 9.471(1), c = 9.939(1) Å, and β = 102.5(2)°. The unit-cell volume V was 513.4(5) Å^3, and the absorption coefficient μ was 0.48 mm^{-1}.

A Nonius CAD-4 diffractometer was used with monochromatedMo$K\alpha$ radiation (λ = 0.7107 Å); $\omega/2\theta$ mode; $2\theta_{max}$ = 60° ($0 \leq h \leq 8, 0 \leq k \leq 13, -13 \leq l \leq 13$). Two reference reflections were used for control and scaling of a small decrease of intensities in the course of the data collection.

From 1375 measured reflections, 600 were observed with $I \geq 3\sigma(I)$. F_{000} = 244. Corrections were made for Lorentz-polarisation effects, but not for extinction and absorption. This last effect was not taken into account because the crystal absorption with Mo radiation was practically negligable.

The structure was solved by direct methods with the MULTAN-80 program[5]; 206 reflections with $|E| > 1.59$ and 5 reflections in the starting set were used to determine the structure; 12 atoms from the 14 contained in the molecule were found. The remainder were obtained from difference Fourier syntheses.

The atomic parameters were refined by full-matrix least squares, using anisotropic temperature factors for all non-H atoms.

All the H atoms were placed in geometrically calculated positions and were assigned the same isotropic thermal parameters as the atoms to which they were bonded.

Refinement was based on F (structure amplitudes) to minimise the function $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$; 127 parameters were refined (9 parameters per atom plus 1 for the scale); the over-determination ratio was 4.7 reflections/parameter. The refinement led to a final convergence with R = 0.088. All parameter shifts during the final cycle of refinement were less than 0.01 σ. Atomic scattering factors were from the International Tables for X-Ray Crystallography[6] and all calculations were carried out with the X-Ray System[7]. The y co-ordinate of S-1 was held fixed in order to define the origin.

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