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# Structure of 1,3-Dihydro-3-methyl-4-(4-thio-β-D-erythrofuranosyl)-1-(*p*-tolyl)-2*H*-imidazole-2-thione, $C_{15}H_{18}N_2O_2S_2$

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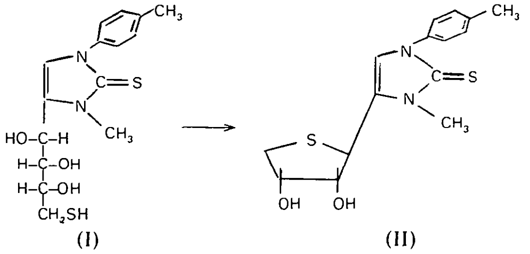
**Abstract.** $M_r = 322{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 11{\cdot}408$ (2), $b = 17{\cdot}502$ (3), $c = 7{\cdot}846$ (2) Å, $V = 1566{\cdot}5$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}36$, $D_m$(flotation in benzene/$CCl_4$) = 1·35 Mg m$^{-3}$, graphite-monochromated Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}36$ mm$^{-1}$, $F(000) = 680$, $T = 293$ K, final $R = 0{\cdot}040$ for 2172 independent reflections. The thiotetrafuranose-ring conformation is intermediate between twist ${}^2_3T$ and envelope $E_3$. The phenyl–imidazole and thiofuranose–imidazole dihedral angles are 46·7 (1) and 52·9 (1)°. The packing of the molecules is governed only by van der Waals contacts.

**Introduction.** Heterocyclic imidazole *C*-nucleosides are interesting because of their structural analogies with natural *C*-nucleosides. Sugars with S in the ring and nucleosides with this modification are not very common. The base—sugar bond in these analogues is more stable towards enzymic cleavage than in the naturally occurring compounds and the substitution of S for O markedly affects the conformation of the sugar ring (McCormick & McElhinney, 1978); interesting biological differences have been observed (Bloch, 1975; Bobek, Bloch, Parthasarathy & Whistler, 1975). The crystal structure of the title compound has been determined as part of a systematic structural investigation of the conformational properties of imidazole *C*-nucleosides with a view to assessing the influence of these sugar moieties on antitumour and antiviral properties. Compound (II) has been obtained by formation of the anhydride of 1,3-dihydro-3-methyl-4-(D-*arabino*-1,2,3-trihydroxy-4-mercaptobutyl)-1-(*p*-tolyl)-2*H*-imidazole-2-thione (I) catalysed by trifluoracetic acid.



(I) (II)

A previous ¹H NMR study in solution (Fernandez-Bolaños, Fuentes-Mota & Fernández-Bolaños Guzmán, 1984) showed the same configuration as obtained by the present X-ray study.

**Experimental.** Single crytals in form of colourless prisms. Crystal approximately 0·29 × 0·20 × 0·49 mm. Preliminary studies indicated orthorhombic symmetry, systematic absences consistent with $P2_12_12_1$. Lattice parameters refined using 25 reflections in the range $6 < \theta < 12°$. Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\omega/2\theta$ mode. $2\theta_{\max} = 60°$ ($h \le 16$, $k \le 24$, $l \le 11$). Two standard reflections (400 and $\bar{4}00$) monitored every 100 reflections showed only statistical fluctuations. 2172

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observed reflections [$I > 2\sigma(I)$] out of 2616 independent reflections measured. $R_{\text{int}} = 0{\cdot}010$ from merging of 8 equivalent reflections. Intensities corrected for Lorentz and polarization effects, but not for absorption ($\mu R = 0{\cdot}091$) or extinction. Structure solved by direct methods with *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). 234 reflections with $E > 1{\cdot}50$ were used and a choice of phasing was possible based on figures of merit. The highest combined figure of merit derived with unit weights for the components was 2·98. An $E$ map computed with this phase set had distinguishable peaks for 19 of 21 non-hydrogen atomic positions; remaining atoms were located from a Fourier synthesis. Refinement on $F$ by full-matrix least squares. Scattering factors from *International Tables for X-ray Crystallography* (1962). A difference Fourier synthesis up to $\sin\theta/\lambda = 0{\cdot}5$ Å$^{-1}$ revealed the H-atom positions; a final least-squares process in a mixed mode including H atoms with isotropic temperature factors equal to those of the attached atoms gave $R = 0{\cdot}040$ and $wR = 0{\cdot}038$ [$w = 1/\sigma^2(F)$]; $S = 2{\cdot}35$. Final difference map showed strongest peak of $\pm 0{\cdot}3$ e Å$^{-3}$. $(\Delta/\sigma)_{\max} = 0{\cdot}3$. Computations performed with the *XRAY*70 system (Stewart, Kundell & Baldwin, 1970).

**Discussion.** Positional and isotropic thermal parameters for the non-hydrogen atoms are given in Table 1.* Bond lengths and angles for non-hydrogen atoms together with their estimated standard deviations are given in Fig. 1. The C—H distances range from 0·799 to 1·036 Å, with an average value of 0·920 Å. The phenyl group is planar, with a maximum deviation from the best plane of 0·009 Å. The average C—C bond is 1·385 (5) Å and C—C—C angle 120·0 (3)°. The two substituent atoms C(15) and N(1) are at −0·038 (4) and −0·155 (3) Å from the plane. The C(15)—C(phenyl) distance of 1·510 (5) Å and the C(8)—N(1) inter-ring distance of 1·435 (4) Å agree with corresponding distances in analogous compounds (Barragan, López-Castro & Márquez, 1977; Criado, Conde & Márquez, 1983; Moreno, López-Castro & Márquez, 1985).

*Imidazole ring.* Bond lengths and angles agree quite well with the mean values reported for analogous imidazole-2-thione compounds (Conde, Moreno & Márquez, 1975). The partial double-bond character of the S—C bond is in agreement with the canonical resonance forms of the thiourea system and is a normal feature of these compounds. The ring is planar, with a

Table 1. *Positional parameters* (×10⁴) *and equivalent isotropic thermal parameters* (×10⁴)

$$U_{\text{eq}} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j\cos(\mathbf{a}_i.\mathbf{a}_j).$$

| | $x$ | $y$ | $z$ | $U_{\text{eq}}$(Å$^2$) |
|---|---|---|---|---|
| S(1) | 3484 (1) | 11323 (1) | 3997 (1) | 467 (3) |
| S(2) | 4273 (1) | 7723 (1) | 6134 (1) | 399 (2) |
| O(1) | 1767 (2) | 8216 (1) | 2902 (3) | 515 (9) |
| O(2) | 1984 (2) | 6910 (1) | 4850 (4) | 596 (10) |
| N(1) | 4976 (2) | 10125 (1) | 4627 (4) | 367 (8) |
| N(2) | 3147 (2) | 9805 (1) | 4586 (3) | 373 (8) |
| C(1) | 3879 (3) | 10413 (1) | 4426 (4) | 361 (9) |
| C(2) | 3782 (2) | 9136 (1) | 4868 (4) | 341 (9) |
| C(3) | 4912 (3) | 9342 (1) | 4887 (5) | 371 (9) |
| C(4) | 3245 (2) | 8365 (1) | 5076 (4) | 322 (8) |
| C(5) | 2899 (3) | 7970 (2) | 3403 (4) | 386 (10) |
| C(6) | 2917 (3) | 7111 (2) | 3755 (5) | 455 (11) |
| C(7) | 4053 (3) | 6936 (2) | 4642 (5) | 514 (13) |
| C(8) | 6076 (3) | 10522 (1) | 4691 (4) | 359 (9) |
| C(9) | 7028 (3) | 10208 (2) | 3852 (5) | 442 (10) |
| C(10) | 8127 (3) | 10537 (1) | 4056 (5) | 462 (11) |
| C(11) | 8280 (3) | 11182 (1) | 5065 (4) | 393 (10) |
| C(12) | 7312 (3) | 11493 (1) | 5861 (4) | 414 (10) |
| C(13) | 6216 (3) | 11174 (1) | 5686 (4) | 395 (10) |
| C(14) | 1874 (3) | 9883 (2) | 4559 (6) | 546 (14) |
| C(15) | 9480 (3) | 11530 (2) | 5307 (6) | 586 (14) |

Table 2. *Selected torsion angles* (°)

| | |
|---|---|
| C(1)—N(2)—C(2)—C(4) | −179·8 (4) |
| C(14)—N(2)—C(2)—C(4) | 4·4 (3) |
| C(5)—C(4)—C(2)—C(3) | −99·0 (4) |
| C(1)—N(1)—C(8)—C(9) | −139·0 (4) |
| S(2)—C(4)—C(2)—N(2) | −160·2 (3) |

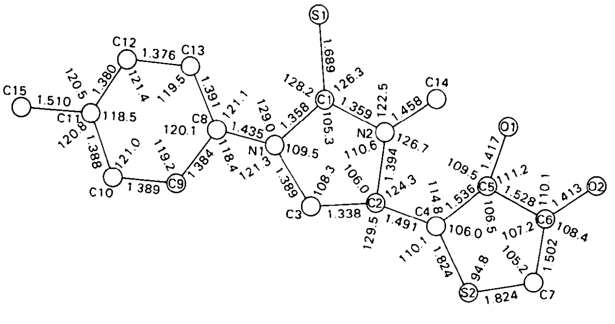

Fig. 1. Interatomic distances (Å) and bond angles (°). Mean standard deviations are 0·004 Å and 0·3°.

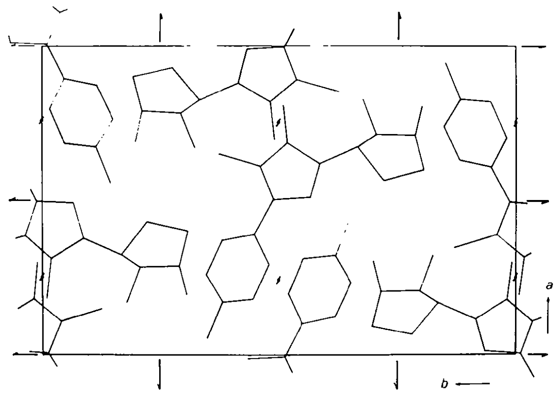

Fig. 2. A view along [001] of the unit-cell contents.

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* Lists of structure factors, anisotropic thermal parameters, distances and angles involving non-H atoms, and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42274 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

maximum deviation from the least-squares plane of 0·004 Å. The four substitutents S(1), C(4), C(8) and C(14) are at 0·065 (1), 0·013 (3), −0·090 (3) and −0·083 (4) Å from the best plane. C(14)—N(2), C(2)—C(4), N(1)—C(8) are 1·458 (4), 1·491 (4) and 1·435 (4) Å. The average angles C—N—C, N—C—C are 110·2 (3) and 107·2 (3)°. The N—C—N angle is 105·3 (2)°.

*Thiotetrafuranose ring.* This compound represents one of the first structural studies of a thiofuranose nucleoside and as expected the substitution of S for O affects markedly the conformation of this ring. The average C—C bond length is 1·522 (5) Å and the distances S(2)—C(4) and S(2)—C(7) are equal and correspond to the S—C value given for a single bond. The average C—C—C, C—C—S and C—S—C endocyclic angles are 106·9 (2), 105·6 (2) and 94·8 (2)°. The thiofuranose ring is not planar. In terms of ring-puckering coordinates (Cremer & Pople, 1975) the amplitude phase magnitudes are $q = 0{\cdot}427\ (4)$ Å and $\varphi = 98{\cdot}2\ (4)°$ for the sequence S(2)—C(4)—C(5)—C(6)—C(7) and the resulting conformation is intermediate between twist ${}^2_3T$ and envelope $E_3$. The phenyl–imidazole, and thiofuranose–imidazole dihedral angles are 46·7 (1) and 52·9 (1)°. These values are rather lower (values range from 60 to 80°) and could indicate a large contribution of crystal forces to the phenyl–imidazole and thiofuranose–imidazole subrotations (Moreno, López-Castro & Márquez, in the press). Table 2 shows the main torsion angles.

The crystal packing, as viewed along the *c* axis is shown in Fig. 2; it is maintained by van der Waals contacts.

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# Structure of an Optically Pure Steroidal Methanesulfinate*

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**Abstract.** 3-Oxo-*A*-norandrostane-5$\beta$,17$\beta$-diol 17-acetate 5-[(*R*)-methanesulfinate], $C_{21}H_{32}O_5S$, $M_r = 396{\cdot}55$, monoclinic, $P2_1$, $a = 12{\cdot}475\ (4)$, $b = 7{\cdot}203\ (1)$, $c = 11{\cdot}510\ (4)$ Å, $\beta = 90{\cdot}80\ (2)°$, $V = 1034{\cdot}2$ Å$^3$, $Z = 2$, $D_m = 1{\cdot}282$, $D_x = 1{\cdot}273$ Mg m$^{-3}$, Cu $K\alpha$, $\lambda(K\alpha_1) = 1{\cdot}54056$ Å, $\mu = 1{\cdot}582$ mm$^{-1}$, $F(000) = 428$, $T = 293$ K, $R = 0{\cdot}029$ for 2239 reflexions with $I \geq 2{\cdot}0\sigma(I)$. The ring junction *A*/*B* is *cis*. The geometry around the S atom, with the lone pair of electrons, is tetrahedral with the *R* chirality. The molecules are linked by C—H···O=S hydrogen bonds into chains along **b**.

**Introduction.** Derivatives of *A*-norandrostane-5,17α-diol were synthesized (Edwards & Grue-Sorensen, 1985) in order to study the behaviour of α-acyl carbocations in steroids (Edwards & Paryzek, 1983) and explore the limits to apparent $S_N2$ displacement at tertiary C atoms adjacent to carbonyl groups (Edwards

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