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5-Chloro-5-deoxy-1,2-O-isopropylidene-3-methanesulphonyl-4-thio- β -L-arabinofuranose

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Abstract. $C_9H_{15}ClO_5S_2$, orthorhombic, $P2_12_12_1$, $a = 8.426$ (9), $b = 9.029$ (14), $c = 17.806$ (21) Å, $Z = 4$, $D_o = 1.46$, $D_c = 1.48$ g cm $^{-3}$. The compound was prepared in the course of a study of sulphur-substituted sugars. Both five-membered rings in the molecule have an envelope conformation. The chloromethyl and methanesulphonyl substituents of the thiofuranose ring are mutually *trans*.

Introduction. Crystals suitable for intensity collection were obtained by recrystallization from diisopropyl ether. Initial cell dimensions were determined from precession photographs (Mo $K\alpha$ radiation); systematic absences ($h00$ for h odd, $0k0$ for k odd, $00l$ for l odd) uniquely determine the space group $P2_12_12_1$.

A crystal $\sim 0.5 \times 0.4 \times 0.4$ mm was sealed in a Lindemann glass tube and mounted on a Hilger-Watts Y290 four-circle diffractometer, with a misaligned a few degrees from the spindle (ϕ) axis. Unit-cell parameters were refined by least-squares calculations, from

12 reflexions ($2\theta > 36^\circ$) (Busing & Levy, 1967). Intensities were collected for all unique reflexions with $2\theta \leq 55^\circ$ (Mo $K\alpha$ radiation, Zr filter, $\lambda = 0.71069$ Å,

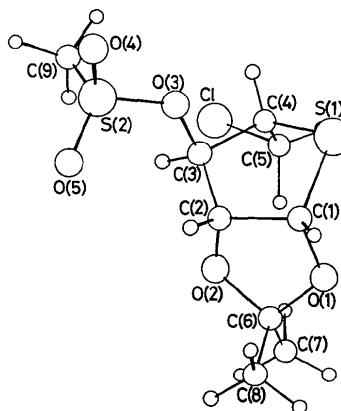


Fig. 1. Perspective view showing the labelling of the non-hydrogen atoms.

Table 1. Atomic coordinates ($\times 10^4$) and anisotropic thermal parameters ($\text{Å}^2 \times 10^4$)

	x	y	z	U_{11} or U	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	3115 (1)	761 (1)	1702 (1)	386 (4)	452 (5)	652 (6)	-9 (4)	124 (4)	84 (4)
C(1)	4866 (4)	81 (4)	2182 (2)	418 (17)	370 (15)	460 (16)	1 (13)	108 (15)	-21 (15)
H(1)	4476	-595	2647	425 (97)					
C(2)	5895 (4)	-737 (3)	1599 (2)	391 (15)	243 (13)	461 (17)	9 (13)	-5 (14)	24 (13)
H(2)	6037	-1893	1741	505 (105)					
C(3)	5147 (4)	-652 (3)	820 (2)	327 (14)	283 (13)	425 (16)	-15 (12)	4 (13)	-15 (13)
H(3)	6091	-588	411	464 (100)					
C(4)	4042 (4)	674 (3)	776 (2)	381 (16)	323 (15)	529 (19)	64 (14)	-12 (15)	26 (14)
H(4)	3216	526	318	517 (103)					
C(5)	4856 (5)	2135 (4)	598 (2)	592 (23)	314 (15)	561 (19)	76 (15)	-25 (18)	17 (17)
H(51)	4035	3036	687	675 (98)					
H(52)	5873	2273	961						
Cl	5496 (2)	2129 (1)	-367 (1)	808 (8)	669 (6)	619 (6)	183 (5)	91 (6)	-59 (6)
O(1)	5841 (3)	1257 (3)	2436 (2)	438 (12)	449 (13)	606 (15)	-202 (12)	114 (12)	-24 (12)
O(2)	7333 (3)	76 (3)	1585 (1)	326 (11)	472 (13)	474 (13)	-126 (11)	28 (10)	-18 (10)
C(6)	7448 (4)	853 (4)	2281 (2)	432 (16)	370 (17)	426 (17)	-98 (14)	37 (14)	-17 (15)
C(7)	8396 (5)	2248 (5)	2169 (2)	566 (22)	488 (19)	671 (23)	-71 (19)	7 (21)	-160 (20)
H(71)	9616	1966	2051	742 (79)					
H(72)	8342	2915	2672						
H(73)	7910	2866	1703						
C(8)	8115 (7)	-126 (5)	2890 (3)	884 (31)	519 (21)	576 (22)	-6 (19)	-205 (24)	11 (25)
H(81)	8188	490	3409	1220 (131)					
H(82)	9286	-497	2730						
H(83)	7349	-1073	2967						
O(3)	4126 (3)	-1936 (2)	711 (1)	336 (10)	305 (11)	500 (12)	-51 (10)	30 (9)	-18 (9)
S(2)	4783 (1)	-3365 (1)	301 (1)	350 (4)	287 (3)	509 (4)	-48 (3)	1 (3)	-4 (3)
O(4)	3498 (3)	-4391 (2)	356 (2)	505 (13)	334 (11)	702 (16)	-17 (12)	5 (14)	-89 (11)
O(5)	6288 (3)	-3749 (3)	604 (2)	438 (13)	484 (15)	738 (17)	-22 (14)	-66 (13)	124 (12)
C(9)	4995 (5)	-2807 (5)	-637 (2)	521 (22)	587 (21)	513 (18)	-79 (18)	66 (18)	-87 (20)
H(91)	5966	-2031	-681	1080 (108)					
H(92)	3912	-2284	-824						
H(93)	5237	-3763	-983						

θ - 2θ scan mode, 2 s count at each of 80 steps of 0.01° in θ , background counts of 40 s at each end of the scan). Three standard reflexions showed no significant decay during the collection.

No absorption corrections were applied ($\mu = 5.86 \text{ cm}^{-1}$). Reflexions with $I < 3\sigma(I)$ were rejected [$\sigma(I)$ based on counting statistics]. 1549 unique reflexions were used for structure solution and refinement. The

structure was solved by multisolution tangent refinement methods (Germain, Main & Woolfson, 1971) and refined by anisotropic full-matrix least-squares calculations, to a minimum value of $\sum w\Delta^2$ [$\Delta = |F_o| - |F_c|$, $w = 1/\sigma^2(F)$]. H atoms were placed in geometrically calculated positions (C-H = 1.08 \AA) and made to ride on the corresponding C atoms during refinement, by keeping the C-H vectors constant in length and direction; the H atoms attached to each C atom had a common isotropic temperature factor, which was refined. Neutral atom scattering factors were those of Cromer & Waber (1974) and Cromer & Ibers (1974). The final value of R was 3.36% ('observed' reflexions only), and $R_2 (= \{\sum w\Delta^2 / \sum wF_o^2\}^{1/2}) = 4.62\%$. The number of parameters refined was 162. Atomic parameters are shown in Table 1.*

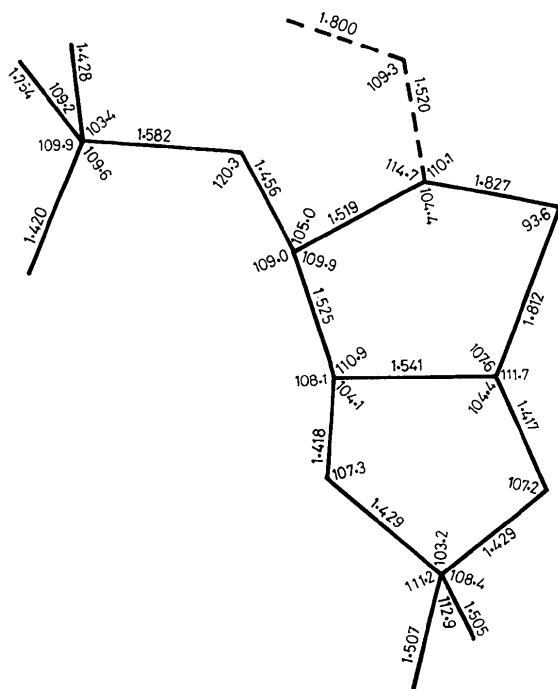


Fig. 2. Bond lengths and angles not involving H atoms. The following angles are not shown: O(3)-S(2)-C(9) 103.9° ; O(4)-S(2)-O(5) 119.5° ; O(2)-C(6)-C(7) 109.3° ; O(1)-C(6)-C(8) 111.4° . E.s.d.'s in bond lengths are 0.003 - 0.006 \AA ; in angles 0.02 - 0.04° . C(5) and Cl have been displaced for greater clarity.

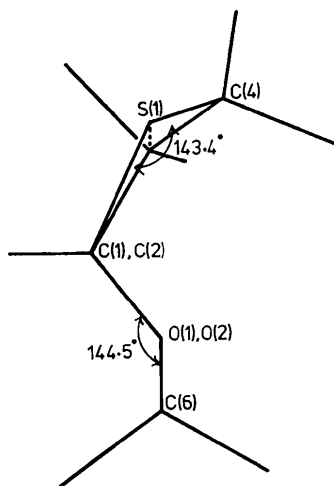


Fig. 3. View down C(1)-C(2) showing the ring conformations.

Discussion. The compound (Fig. 1) was prepared by ring contraction of a 5-thiopentopyranose sulphonate (Clegg, Hughes & Wood, 1975). The relative positions of the chloromethyl and methanesulphonyl substituents (*cis* or *trans*) could not be determined with certainty from the ^1H n.m.r. spectrum, and the crystal structure determination was undertaken. The absolute configuration was deduced from the synthesis. The two substituents are found to be mutually *trans*.

The two five-membered rings have envelope conformations, as shown by a projection down C(1)-C(2) (Fig. 3). The two 'flap' angles (defined as angles between least-squares planes fitted to the atoms concerned) are very similar, but the thiofuranose flap is *endo*, while the isopropylidene flap is *exo*. Bond lengths and angles are shown in Fig. 2.

Rotational conformation about bonds is either constrained by ring geometry, or assumed to be staggered for the geometric placing of the H atoms, except for C(4)-C(5), O(3)-S(2) and O(3)-C(3). The conformation about C(4)-C(5) is staggered [torsion angles are Cl-C(5)-C(4)-C(3) 71.3° , Cl-C(5)-C(4)-S(1) -171.3° (Allen & Rogers, 1969)]; the conformation about O(3)-S(2) is such that C(3) is staggered between O(5) and C(9) [C(3)-O(3)-S(2)-O(5) 47.2° , C(3)-O(3)-S(2)-C(9) -70.3° , C(3)-O(3)-S(2)-O(4) 175.7°]; about O(3)-C(3), the conformation is even further from ideal staggering [S(2)-O(3)-C(3)-C(4) 147.4° , S(2)-O(3)-C(3)-C(2) -94.9° , S(2)-O(3)-C(3)-H(3) 25.3°]. Clearly, these conformations result from the balance between intra- and inter-molecular forces.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31238 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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 β -Flupenthixol

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Abstract. β -Flupenthixol; *trans* form of 2 trifluoromethyl-9-[3-[4-(β -hydroxyethyl)-1-piperazinyl]propylidene]thioxanthene, C₂₃H₂₅N₂OF₃S, *M* = 434.51, monoclinic, *P*2₁/*c*, *a* = 9.011 (2), *b* = 15.218 (3), *c* = 18.493 (4) Å, β = 120.37 (1)°, *D*_x = 1.32, *D*_c = 1.31 g cm⁻³, *Z* = 4. The dihedral angle of the thioxanthene moiety is 143.1° and an intramolecular hydrogen bond is formed between the hydroxyl group and a piperazinyl N atom. There is evidence of thermal disorder toward the side-chain extremity.

Introduction. Space group and preliminary cell parameters were determined from precession and Weissenberg photographs. Systematic absences were *h*0*l*, *l* odd; 0*k*0, *k* odd; space group *P*2₁/*c*. A crystal 0.70 × 0.75 × 0.70 mm was mounted, with **b** parallel to the φ axis of a Picker card-controlled four-circle diffractometer. Data were collected throughout the range 4° ≤ 2 θ ≤ 120° with graphite-monochromated Cu *K* α radiation (λ = 1.54178 Å) with a θ -2 θ scan operating at 2° min⁻¹ in 2 θ , and of 3472 independent observations, 2308 had *I* ≥ 4 σ (*I*) and were used in subsequent stages. Scaling, with respect to monitor reflexion values, and Lorentz and polarization corrections were applied. No correction was made for absorption (μ = 15.7 cm⁻¹).

The structure was solved by multi-solution direct methods (Sheldrick, 1975) with 567 *E* values ≥ 1.4. The 'best' *E* map revealed sites for all but three of the non-hydrogen atoms, and those remaining were located on a subsequent difference map. Six cycles of full-

matrix least-squares isotropic refinement yielded an *R* of 0.18 and indicated two regions of high thermal motion, one involving the -CF₃ group and the other, between the piperazine ring and hydroxyl O atom, at C(23) and C(24). The behaviour of F atoms during refinement was markedly improved by allocating an occupancy of 0.85 to the major F positions, and of 0.15 to secondary positions, F(*nn*) in Table 1, which were found in a difference map. A difference synthesis, calculated with C(23) and C(24) omitted showed, in that region, an elongated ellipsoid of electron density extending for *ca* 2.5 Å in which two very diffuse maxima were embedded. No chemically reasonable model could be chosen to describe the effect and these two atoms were, therefore, allowed unrestricted refinement, but with resultant unreliability in associated bond parameters. All atoms {except F(*nn*) which remained isotropic} were then refined with anisotropic thermal parameters, and following six cycles *R* was 0.081. A difference synthesis then showed H atoms at all the expected sites, apart from C(23) and C(24), and refinement was continued with H atoms included. Positional and isotropic thermal parameters for the H atoms were refined in all but four cases, these requiring to be constrained so that respective C-H vectors retained their original magnitude and direction. Convergence was attained after eight cycles at an *R* of 0.063 for 2308 reflexions.‡ The function minimized was $\sum w\{|F_o| - |F_c|\}^2$ where $w = 1/\sigma^2(F)$ and the final $R_w = \sum w^{1/2}\{|F_o| - |F_c|\} / \sum w^{1/2}|F_o| = 0.063$. Final atomic parameters are presented in Tables 1 and 2.

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‡ A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31198 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.