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Note

X-Ray structure of (5*S*,8*R*,9*R*,10*S*)-8,9,10-triacetoxy-3-acetyl-1,6-dioxa-3-azaspiro[4.5]decane, a spiropyranose derivative

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(5*S*,8*R*,9*R*,10*S*)-8,9,10-Triacetoxy-3-acetyl-1,6-dioxa-3-azaspiro[4.5]decane was obtained[1] by reaction of 1-amino-1-deoxy-D-*arabino*-hexulose acetate with carbon sulphide at 75° followed by treatment with acetic anhydride and pyridine. The structures **1** and **2** were suggested for the oxazole ring, based on polarimetry and u.v., i.r., and ^{1}H- and ^{13}C-n.m.r. data. The present X-ray analysis elucidated the structure as **1** (Fig. 1).

The bond lengths and angles are shown in Table I, and an ORTEP diagram of the molecule with the atom numbering is shown in Fig. 1.

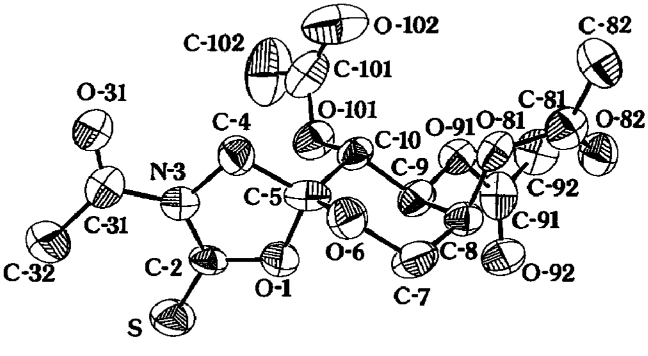

Fig. 1. An ORTEP diagram of molecule **1** with atomic numbering. Thermal ellipsoids enclose 50% probability.

The five-membered ring is planar (maximum deviation from the least-squares plane 0.024 Å) and the substituents S-1 and C-31 are at 0.165(5) and −0.243(16) Å, respectively, from the least-squares plane. The acetyl groups are also planar (maximum deviation from the least-squares plane 0.023 Å). This planarity allows the torsion angles H–C_{ring}–O–(acetate) to be used as a measure of the orientation of the acetate with

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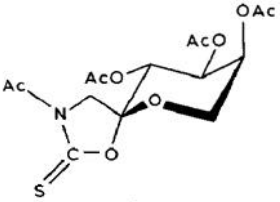
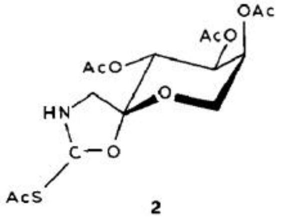


1



2

respect to the adjacent C_{ring}–H. The three torsion angles are 25(2)°, −46(2)°, and 0(2)°. The C–C distances in the pyranose ring are in the range 1.488(19)–1.517(18) Å. The glycosidic C–O linkages are 1.460(17) and 1.385(16) Å, and the shortening of the latter reflects the anomeric effect[2,3]. The exocyclic C_{ring}–O bond lengths have a mean value of 1.444(15) Å and are longer than the average value of 1.426 Å for other non-acetylated glycosyl residues[4]. The interior and exterior ring angles are in the range 107.2–112.0° consistent with the expected high degree of tetrahedral character. The angles at the O atoms linked to the acetate groups have a mean value of 106.5(10)°. The three O–C (=O)–C(methyl) angles are 110.6(11)°, 110.8(12), and 112.1(14)°, and accord with the value[5] of 111°.

The pyranose ring in the crystal is in a chair conformation. Puckering parameters[6] for the atomic sequence O-6, C-7, C-8, C-9, C-10, C-5 are θ 173(1)°, ψ 13(10)°, and Q 56(1)Å. The asymmetric parameters[7] are ΔCs[O-6] 0.11(6) and ΔC2[C-7–O-6] 0.009(5). The substituents C-4, O-101, and O-91 are equatorial, and O-1 and O-81 are axial.

The crystal packing is governed by van der Waals forces.

EXPERIMENTAL*

The crystal used {m.p. 121°, $[\alpha]_D^{22}$ −220° (*c* 1, chloroform)} was 0.15 × 0.10 × 0.15 mm and belonged to the orthorhombic system with systematic absences consistent with $P2_12_12_1$. The lattice parameters, refined using 25 reflections within the range $2 < \theta < 12°$, were *a* 11.176(3), *b* 20.833(5), and *c* 8.135(3) Å. The unit cell volume *V* was 1894(1) Å^3 and the absorption coefficient was 0.206 mm^{-1}.

An Enraf–Nonius CAD-4 diffractometer was used with monochromated Mo-K_α radiation (0.7107 Å), and the $\omega/2\theta$ scan technique, at room temperature ($h \leqslant 14, k \leqslant 27, l \leqslant 10$). Two standard reflections (372 and $\bar{3}7\bar{2}$), monitored every 100 reflections, showed only statistical fluctuations. From 1932 unique reflections measured [sin (θ/λ) max = 0.60 Å], 1639 were observed with $I \geqslant 2\sigma(I)$. *F*(000) was 816. Corrections were made for Lorentz-polarization effects, but not for extinction and absorption.

The structure was solved by direct methods using the MULTAN 80 program[8]. Positional and anisotropic thermal parameters for all non-hydrogen atoms were refined

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* Supplementary data have been deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA|DD|450|*Carbohydr. Res.*, 209 (1991) 285–288.

TABLE I

Bond lengths (Å) and angles (°)

S–C-2	1.605(12)	O-102–C-101	1.211(20)
O-1–C-2	1.341(14)	N-3–C-2	1.385(16)
O-1–C-5	1.454(15)	N-3–C-4	1.462(16)
O-6–C-5	1.385(16)	N-3–C-31	1.421(18)
O-6–C-7	1.460(17)	C-4–C-5	1.535(18)
O-31–C-31	1.200(18)	C-5–C-10	1.517(17)
O-81–C-8	1.452(14)	C-7–C-8	1.488(18)
O-81–C-81	1.340(15)	C-8–C-9	1.517(17)
O-82–C-82	1.206(16)	C-9–C-10	1.502(17)
O-91–C-9	1.445(14)	C-31–C-32	1.497(20)
O-91–C-91	1.382(15)	C-81–C-82	1.488(20)
O-92–C-91	1.202(18)	C-91–C-92	1.458(21)
O-101–C-10	1.435(14)	C-101–C-102	1.488(25)
O-101–C-101	1.358(18)		
C-2–O-1–C-5	112.4(9)	C-7–C-8–C-9	108.9(10)
C-5–O-6–C-7	114.4(10)	C-81–C-8–C-9	110.2(9)
C-8–O-81–C-81	117.4(9)	O-91–C-9–C-8	112.0(9)
C-9–O-91–C-91	114.0(9)	C-8–C-9–C-10	109.4(10)
C-10–O-101–C-101	118.3(10)	C-91–C-9–C-10	107.1(9)
C-4–N-3–C-31	116.7(10)	C-5–C-10–C-9	109.1(9)
C-2–N-2–C-31	130.7(10)	C-101–C-10–C-9	109.1(9)
C-2–N-3–C-4	111.8(10)	C-101–C-10–C-5	108.2(9)
O-1–C-2–N-3	108.7(9)	O-31–C-31–N-3	116.5(12)
S–C-2–N-3	130.8(9)	N-3–C-31–O-32	117.2(12)
S–C-2–O-1	120.4(9)	O-31–C-31–C-32	126.1(14)
N-3–C-4–C-5	102.7(9)	O-81–C-81–C-82	125.0(11)
O-6–C-5–C-4	108.9(11)	O-82–C-81–O-82	124.3(12)
O-1–C-5–C-4	104.2(9)	O-81–C-81–C-82	110.6(11)
O-1–C-5–C-6	109.8(9)	O-91–C-91–O-92	122.3(12)
C-4–C-5–C-10	114.6(10)	O-92–C-91–C-92	126.6(14)
O-6–C-5–C-10	111.7(10)	O-91–C-91–C-92	110.8(12)
O-1–C-5–C-10	107.1(10)	O-101–C-101–O-102	121.3(14)
O-6–C-7–C-8	112.6(10)	O-102–C-101–C-102	126.3(16)
O-81–C-8–C-7	107.6(9)	O-105–C-101–C-102	112.1(14)

by full-matrix least squares; difference Fourier synthesis revealed the H atoms.

All of the H atoms were assigned the same isotropic temperature factors as the atoms to which they were bonded, and were included in the refinement with positional and thermal parameters fixed (235 parameters). Refinement was based on F(structure amplitudes) to minimise the function $\Sigma w(|F_o|-|F_c|)^2$ with $w = 1/\sigma^2(F_o)$.

The refinement led to a final convergence with $R=0.07$. All shifts of parameters during the final cycle of refinement were <0.02; the residual electron density in the difference map was ± 0.3 eÅ^{-3}.

The uncommonly high R factor and e.s.d.'s, as well as the discrepancies between F_o and F_c, seem to be due to the poor quality of the crystals. Atomic scattering factors were from International Tables for X-Ray Crystallography[9] and all calculations were carried out with the X-Ray System[10].

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