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Note

Crystal and molecular structure of *N*-(2,2-diethoxycarbonylvinyl)-α-D-ribofuranosylamine

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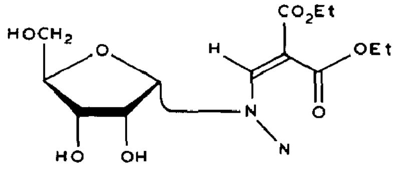
The glycosylamines are of synthetic, biological, and pharmaceutical interest[1]. *N*-(2,2-Diethoxycarbonylvinyl)-α-D-ribofuranosylamine (**1**) was prepared from D-ribosylamine[2], using the method described for other glycosylamines[3,4]. The structure was assigned on the basis of ^{1}H-n.m.r. data, but the configuration could not be deduced; hence, an X-ray analysis has been carried out in order to confirm the structure and determine the anomeric configuration.



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The bond lengths and angles for **1** are given in Table I, and an ORTEP[5] stereoview of the molecule with the atom numbering is shown in Fig. 1. The C–H distances range from 0.977 to 1.046 Å with an average value of 1.014 Å. The average O–H distance is 1.008 Å.

There is extensive electron delocalisation that involves the donor N-1 and the acceptor ethoxycarbonyl groups, as reflected in the molecular dimensions. The C = C bond distance is 1.378 (14) Å, which is much longer than that [1.336(2) Å] in ethylene[6]. There is a corresponding shortening of the N-1–C-6 bond [1.319(11) Å, *cf.* 1.452(2) Å for an N–C (sp^2) bond[7]]. On the acceptor side, the C-7–C-8 and C-7–C-11 bond lengths

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TABLE I

Bond lengths (Å) and angles (°) for **1**

O-4–C-4	1.401(9)	N-1–C-1	1.428(12)
O-4–C-1	1.433(11)	N-1–C-6	1.319(11)
O-3–C-3	1.372(9)	C-4–C-3	1.543(11)
O-2–C-2	1.423(10)	C-4–C-5	1.503(12)
O-8–C-8	1.210(12)	C-3–C-2	1.552(12)
O-6–C-8	1.321(13)	C-2–C-1	1.512(12)
O-6–C-9	1.455(15)	C-6–C-7	1.378(14)
O-11–C-11	1.202(14)	C-7–C-8	1.460(13)
O-7–C-11	1.321(14)	C-7–C-11	1.457(13)
O-7–C-12	1.425(14)	C-9–C-10	1.483(20)
O-5–C-5	1.416(11)	C-12–C-13	1.464(20)
C-4–O-4–C-1	110.3(6)	O-4–C-1–N-1	109.5(8)
C-8–O-6–C-9	118.0(8)	N-1–C-6–C-7	129.2(8)
C-11–O-7–C-12	117.4(9)	C-6–C-7–C-11	113.9(9)
C-1–N-1–C-6	119.6(7)	C-6–C-7–C-8	118.6(8)
O-4–C-4–C-5	110.4(6)	C-8–C-7–C-11	127.5(9)
O-4–C-4–C-3	105.1(6)	O-6–C-8–C-7	113.7(8)
C-3–C-4–C-5	112.1(7)	O-8–C-8–C-7	123.4(9)
O-3–C-3–C-4	115.8(6)	O-8–C-8–O-6	122.9(9)
C-4–C-3–C-2	99.7(6)	O-6–C-9–C-10	106.8(10)
O-3–C-3–C-2	116.2(6)	O-7–C-11–C-7	115.9(9)
O-2–C-2–C-3	110.2(6)	O-11–C-11–C-7	122.7(10)
C-3–C-2–C-1	101.1(7)	O-11–C-11–O-7	121.3(9)
O-2–C-2–C-1	108.6(7)	O-7–C-12–C-13	108.4(10)
N-1–C-1–C-2	114.1(7)	O-5–C-5–C-4	111.6(7)
O-4–C-1–C-2	107.0(7)		

are 1.460(13) and 1.457(13) Å, respectively, which are shorter than that [1.487(5) Å] for a C(sp^2)–C(sp^2) single bond[8]. The dicarbonylvinylamino group has the *E* configuration and is planar (maximum deviation 0.059 Å), and the two ethoxycarbonyl groups are tilted by 5.3(4) and 5.0(4)°. Torsion angles around C-6–C-7 are 176.8(9) and −3.5(15)°, which reflect the small distortion of this group.

The ethoxycarbonyl groups are planar [maximum deviation 0.026(12) Å]. The C–C distances in the furanoid ring are in the range 1.512(12)–1.552(12) Å, in good agreement with those observed for related structures[9,10]. The C-1–O-4 bond is significantly longer than the C-4–O-4 bond, the shortening of which is characteristic[9,11]. The ring C–O bonds have a mean length of 1.417(11) Å, whereas the exocyclic C–OH bonds have a mean length of 1.398(10) Å. The average values of the C–C–C, C–C–O, and C–O–C endocyclic angles are 100.4(6), 106.1(7), and 110.3(6)°, respectively.

The furanoid ring [ϕ 258(1)°] is in the twist conformation and the twist axis passes through the ring oxygen. The puckering amplitude[12] for the ring is 0.40(1) Å. The torsion angles O-4–C-1–C-2–O-2, C-1–O-4–C-4–C-5, O-4–C-4–C-3–O-3, and C-4–O-4–C-1–N-1 are 88.3(8), 142.9(7), −163.1(6), and 128.2(7)°, respectively. The atoms N-1, O-2, and O-3 are on the same side of the best plane through the furanoid ring at

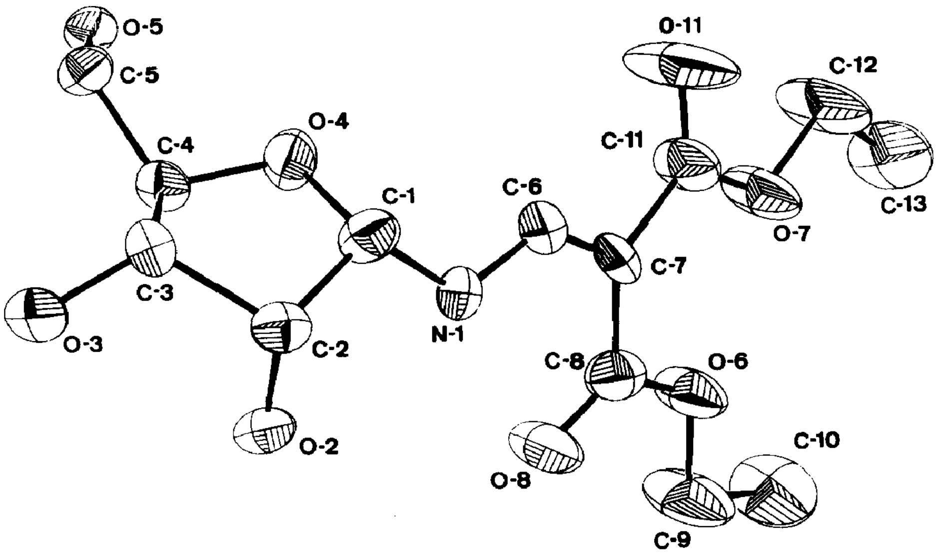

Fig. 1. A stereoview of the molecule of **1**, showing the atomic numbering. Thermal ellipsoids enclose 50% probability.

0.74, 1.63, and 0.24 Å, respectively, and C-5 is on the opposite side at 0.54 Å, which confirms the α configuration.

The packing of the molecules is governed by van der Waals interactions and there are three possible intermolecular hydrogen bonds: O-2···O-3 [2.778(8) Å], O-5···O-3 [2.697(8) Å], and O-5···O-8 [2.731(8) Å]. There is one intramolecular hydrogen bond, namely, N-1···O-8 [2.698(11) Å], which reflects the chelated structure.

EXPERIMENTAL*

The crystal[4] used was 0.40 × 0.08 × 0.60 mm {m.p. 154–156°, $[\alpha]_D^{21}$ +41° (*c* 0.5, pyridine)} and belongs to the orthorhombic system with systematic absences consistent with $P2_12_12_1$. The lattice parameters, refined using 25 reflections within the range $4 < \theta < 12°$, were $a = 8.107(2)$, $b = 38.271(8)$, and $c = 4.994(2)$ Å. The unit cell volume V was 1549.5(8) $Å^3$ and the absorption coefficient was 0.107 mm^{-1}.

An Enraf–Nonius CAD-4 diffractometer was used with monochromated Mo-K_α radiation (0.7107 Å) and an $\omega/2\theta$ scan technique at room temperature, ($h \leqslant 8, k \leqslant 42, l$

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* Lists of the atomic co-ordinates and thermal parameters are 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/470/*Carbohydr. Res.*, 219 (1991) 223–227.

$\leqslant 5$). Two standard reflections (161 and $\bar{1}\bar{6}1$), monitored every 100 reflections, showed only statistical fluctuations. From 1457 unique reflections measured [(sin θ/λ)max = 0.60 Å], 1155 were observed with $I \geqslant 2\sigma(I)$, and $F(000) = 680$. Corrections were made for Lorentz-polarisation effects, but not for extinction and absorption.

The structure was solved by direct methods, using the MULTAN 80 program[13]. Positional and anisotropic thermal parameters for all non-hydrogen atoms were refined 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 included in the refinement with positional and thermal parameters fixed (199 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 parameter shifts during the final cycle of refinement were <0.08; the residual electron density in the difference map was ± 0.3 e Å^{-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[14] and all calculations were carried out with the X-Ray System[15].

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REFERENCES

1 H. Paulsen and K. W. Pflughaupt, in W. Pigman and D. Horton (Eds.), *The Carbohydrates: Chemistry and Biochemistry*, Vol. IB, Academic Press, London, 1980, pp. 881–927.
2 N. J. Cusack, B. J. Hildick, D. H. Robinson, P. N. Rugg, and G. Shaw, *J. Chem. Soc., Perkin Trans. 1*, (1973) 1730–1731, and references therein.
3 A. Gomez Sanchez, M. Gomez Guillen, A. Cert Ventula, and U. Scheidegger, *An. Quim., Ser. B*, 64 (1968) 579–590.
4 J. Fuentes Mota, M. A. Pradera Adrian, C. Ortiz Mellet, J. M. Garcia Fernandez, R. Babiano Caballero, and J. A. Galbis Perez, *Carbohydr. Res.*, 173 (1988) 1–16.
5 C. K. Johnson, *ORTEP II*, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, U.S.A., 1976.
6 L. C. Bartell, E. A. Roth, C. D. Hollowell, K. Kuchitsu, and J. E. Young, *J. Chem. Phys.*, 42 (1965) 2683–2686.
7 H. L. Ammon, P. H. Mazzocchi, M. C. Regan, and E. Colicelli, *Acta Crystallogr., Sect. B*, 35 (1979) 1722–1724.
8 U. Shmueli, H. Shanan-Atidi, H. Horwitz, and Y. Shvo, *J. Chem. Soc., Perkin Trans. 2*, (1973) 657–662.
9 G. A. Jeffrey and A. D. French, *Chem. Soc. Spec. Publ.*, 6 (1978) 183–223.
10 M. J. Dianez, A. Lopez-Castro, and Rafael Marquez, *Acta Crystallogr., Sect. C*, 43 (1987) 558–560.
11 T. Taga, S. Sumiya, K. Osaki, T. Utamura and K. Koizumi. *Acta Crystallogr., Sect. B*, 37 (1981) 963–966.
12 D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, 97 (1975) 1354–1358.

13 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, *Multan80, A system of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*, Universities of York (England) and Louvain (Belgium), 1980.

14 *International Tables for X-ray Crystallography*, Vol. III, Kynoch Press, Birmingham, 1962, pp. 202–207.

15 J. M. Stewart, F. A. Kundell, and J. C. Baldwin, *The X-Ray System*, Computer Science Center, University of Maryland, College Park, 1970.