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Note

Crystal and molecular structure of 3-acetamido-2,6-anhydro-1,3-dideoxy-1-nitro-D-*glycero*-D-*gulo*-heptitol (2-acetamido-2-deoxy-β-D-glucopyranosylnitromethane) monohydrate

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Addition of nitromethane to aldoses in the presence of a base yields a mixture of epimeric nitroalditols[1] which can be cyclodehydrated by simple heating in water to a mixture of anhydronitroalditols (glycosylnitromethanes)[2]. In many cases, the thermodynamically most favoured isomer, the β-glycopyranosylnitromethane, can be obtained in moderate to high yields by direct crystallisation. Reaction of 2-acetamido-2-deoxy-D-glucose thus led to the title compound[3] **1**.

Suitable crystals of **1** for X-ray investigation were obtained as the monohydrate from moist ethanol. Relevant crystallographic data are given in Table I. The structure was solved by direct methods with the program SHELXS-90[4] and refined with SHELXL-92[5].

The refinement was done on F^2 for all reflections. The observed threshold $I > 2\sigma(I)$ is used only for calculating R_{obs}.

All atoms, hydrogens included, were refined. The final fractional co-ordinates of C, N, and O with equivalent isotropic thermal parameters are listed in Table II **. Selected torsion angles are given in Table III, and a perspective view (SCHAKAL-88 plot[6]) of **1** is presented in Fig. 1. The six-membered ring adopts

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** Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre. The coordinates may be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

TABLE I

Crystallographic data for the monohydrate of **1** [a]

Formula	$C_9H_{16}O_7N_2 \cdot H_2O$
Mol wt	264.23 · 18.02
Mp (°C)	203
Crystal dimensions (mm)	0.5 × 0.3 × 0.3
Space group	$P2_1$
Cell parameters (pm, degrees)	
a	503.1(1)
b	798.4(3)
c	1628.4(3)
β	93.23(3)
Volume *V* (pm^3)	$653.0(3) \times 10^6$
Z	2
F (000)	300
Calculated density D_x ($g\ cm^{-3}$)	1.435
λ (Mo$K\alpha$) (pm)	70.9261
μ (cm^{-1})	1.27
2 θ range (degrees)	5 – 50
Reflections measured	4738
Symmetry independent reflections	2298
Reflections with $I > 2\ \sigma\ (I)$	2149
Number of refined parameters	201
Final residual factor *R*	0.038
Goodness of fit *S*	1.067
Diffractometer	Hilger & Watts (Y290)

[a] Standard deviations in parentheses.

TABLE II

Fractional positional parameters ($\times 10^4$) and temperature factors U_{eq} [a] ($\times 10^3$) of carbon, oxygen, and nitrogen atoms for the monohydrate of **1** [b]

Atom	*x*	*y*	*z*	U_{eq}
O-2	1155(3)	9164(2)	7222(1)	32(1)
O-4	2891(4)	5131(2)	8751(1)	46(1)
O-5	195(4)	7934(2)	9350(1)	48(1)
O-7	2585(4)	11648(2)	8468(1)	44(1)
O-11	−1796(4)	9104(3)	5534(1)	65(1)
O-12	1701(5)	9529(4)	4893(1)	77(1)
O-31	6861(3)	4359(2)	6984(1)	46(1)
O-10 (water)	6952(4)	5525(2)	9926(1)	48(1)
N-1	533(4)	8871(2)	5437(1)	38(1)
N-3	2422(3)	4640(2)	6981(1)	29(1)
C-1	2128(4)	7731(3)	6009(1)	33(1)
C-2	955(4)	7568(2)	6833(1)	27(1)
C-3	2495(4)	6272(2)	7366(1)	28(1)
C-4	1373(5)	6217(2)	8220(1)	32(1)
C-5	1435(5)	7969(2)	8589(1)	31(1)
C-6	−15(4)	9193(2)	8000(1)	30(1)
C-7	−11(5)	10994(3)	8296(2)	40(1)
C-31	4631(4)	3807(2)	6804(1)	30(1)
C-32	4223(5)	2179(3)	6363(2)	43(1)

[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$. [b] Standard deviations in parentheses.

TABLE III

Selected torsion angles (deg) in the monohydrate of **1**[a]

Angles in the pyranoid ring		*Angles around the nitro group*	
O-2–C-2–C-3–C-4	58.2(2)	N-1–C-1–C-2–O-2	−66.0(2)
C-2–C-3–C-4–C-5	−55.1(2)	N-1–C-1–C-2–C-3	174.8(2)
C-3–C-4–C-5–C-6	54.5(2)	O-12–N-1–C-1–H-12	34.2(3)
C-4–C-5–C-6–O-2	−56.9(2)	O-11–N-1–C-1–H-12	−145.2(3)
C-5–C-6–O-2–C-2	62.1(2)		
C-6–O-2–C-2–C-3	−62.7(2)		
Angles between vicinal ring substituents (C, O, N)		*Angles between vicinal hydrogens*	
C-1–C-2–C-3–N-3	−60.0(2)	H-11–C-1–C-2–H-2	−67.9(3)
N-3–C-3–C-4–O-4	61.2(2)	H-12–C-1–C-2–H-2	174.6(3)
O-4–C-4–C-5–O-5	−63.2(2)	H-2–C-2–C-3–H-3	−179.9(4)
O-5–C-5–C-6–C-7	61.4(2)	H-3–C-3–C-4–H-4	−178.0(2)
		H-4–C-4–C-5–H-5	175.2(2)
		H-5–C-5–C-6–H-6	−179.2(2)
		H-6–C-6–C-7–H-71	−61.0(3)
		H-6–C-6–C-7–H-71	56.2(3)

[a] Standard deviations in parentheses.

the expected chair conformation [puckering parameters[7]: $Q = 58.7(2)$ pm, $\theta = 2.5(2)°$, $\phi = 40(7)°$]. The nitro group is found in the position usually observed in β-glycopyranosylnitromethanes[8] with N-1 *gauche* to O-2 and *trans* to C-3. The orientations of the oxygen atoms at N-1 correspond to those observed in other

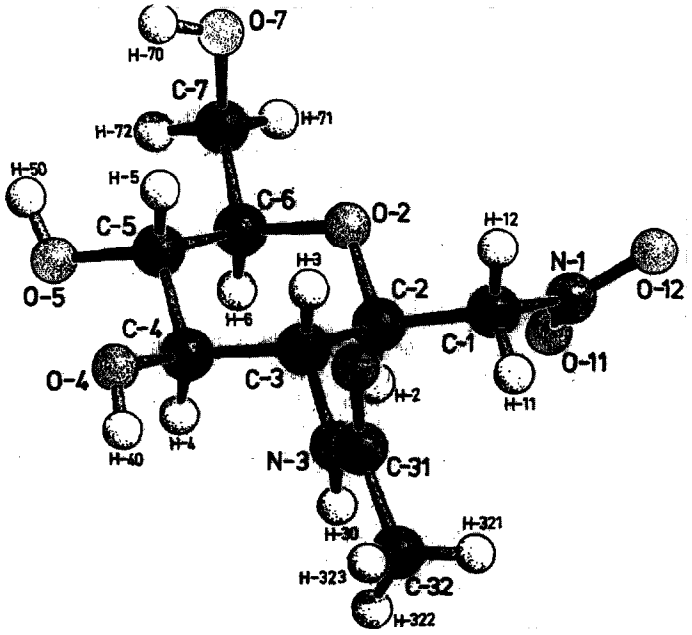

Fig. 1. SCHAKAL-88[6] plot of **1** showing atom numbering.

TABLE IV

Hydrogen-bond pattern [a] in the hydrate of 1 (bond lengths in pm, angles in degrees)

Distances D–H···A	Symmetry operation on A	Distance D···A	Angle D–H···A
N-3 88(1) H-30 ··· 204(1) ··· O-31	$x-1, y, z$	280.7(2)	145(1)
O-4 85(1) H-40 ··· 199(1) ··· O-7	$x, y-1, z$	282.1(2)	167(2)
O-5 85(2) H-50 ··· 193(3) ··· O-10	$-x+1, 1/2+y, -z+2$	274.6(3)	161(2)
O-7 85(1) H-70 ··· 195(2) ··· O-10	$-x+1, 1/2+y, -z+2$	276.2(3)	160(2)
O-10 94(3) H-101 ··· 180(3) ··· O-4	x, y, z	273.7(3)	171(3)
O-10 90(5) H-102 ··· 183(5) ··· O-5	$x+1, y, z$	272.2(3)	175(4)

[a] Standard deviations in parentheses.

nitroalditols[8,9]: O-12 is more or less 1,2-parallel to H-12 and O-11 is 1,3-parallel to H-2. The orientation of the primary hydroxyl group is $-g$, $+g$.

The molecules of **1** are interlinked in the crystal by a complex network of hydrogen bonds, which also involves the molecule of water (Table IV). The hydroxyl hydrogens and the hydrogens of the water all act as donors and the respective oxygens all as acceptors. The N–H group is a donor only, with the carbonyl oxygen as acceptor.

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REFERENCES

1 J.C. Sowden and H.O.L. Fischer, *J. Am. Chem. Soc.*, 66 (1944) 1312–1314; P. Köll, C. Stenns, W. Seelhorst, and H. Brandenburg, *Liebigs Ann. Chem.*, (1991) 201–206.
2 J.C. Sowden and H.O.L. Fischer, *J. Am. Chem. Soc.*, 68 (1946) 1511–1513; *ibid.*, 69 (1947) 1048–1050; J.C. Sowden and M.L. Oftedahl, *J. Org. Chem.*, 26 (1961) 1974–1977; L. Hough and S. Shute, *J. Chem. Soc.*, (1962) 4633–4637; J.C. Sowden, C.A. Bowers, and K.O. Lloyd, *J. Org. Chem.*, 29 (1964) 130–132; L. Petruš, S. Bystrický, T. Sticzay, and V. Bílik, *Chem. Zvesti*, 36 (1982) 103–110; A. Förtsch, H. Kogelberg, and P. Köll, *Carbohydr. Res.*, 164 (1987) 391–402.
3 M. Petrušová, M. Fedoronko, and L. Petruš, *Chem. Zvesti*, 44 (1990) 267–271.
4 G.M. Sheldrick, SHELXS-90, *Acta Crystallogr., Sect. A*, 46 (1990) 467–473.
5 G.M. Sheldrick, SHELXL-92, *Crystal structure refinement*, University of Göttingen, Germany, 1992 (Beta-Test Version).
6 E. Keller, SCHAKAL, *Chem. Unserer Zeit*, 14 (1980) 56–60.
7 D. Cremer and J.A. Pople, *J. Am. Chem. Soc.*, 97 (1975) 1354–1358.

8 P. Köll, J. Kopf, D. Wess, and H. Brandenburg, *Liebigs Ann. Chem.*, (1988) 685–693; J. Kopf, C. Topf, and P. Köll, *Carbohydr. Res.*, 186 (1989) 1–28; J. Kopf, M. Morf, B. Zimmer, O. Jarchow, H. Brandenburg, and P. Köll, *ibid.*, 208 (1990) 1–13.
9 J. Kopf, H. Brandenburg, W. Seelhorst, and P. Köll, *Carbohydr. Res.*, 200 (1990) 339–354; P. Köll, B. Malzahn, and J. Kopf, *ibid.*, 205 (1990) 1–17.