

1-Deoxy-1-(*N*-methyl-4-fluorophenylamino)-*D*-arabino-hexulose

Valeri V. Mossine,^{a*} Charles L. Barnes^b and Thomas P. Mawhinney^c

^aDepartment of Biochemistry, University of Missouri, Columbia, MO65211, USA, ^bDepartment of Chemistry, University of Missouri, Columbia, MO65211, USA, and ^cDepartment of Biochemistry, University of Missouri, Columbia, MO 65211, USA. *Correspondence e-mail: mossinev@missouri.edu

Received 21 February 2018

Accepted 2 March 2018

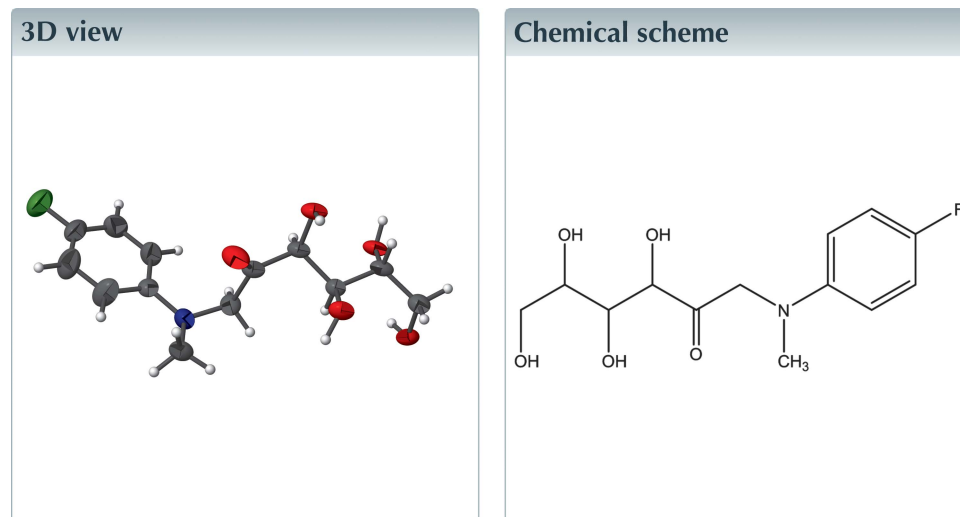
Edited by A. J. Lough, University of Toronto, Canada

Keywords: crystal structure; *D*-fructosamine; acyclic carbohydrate; hydrogen bonding.

CCDC reference: 753227

Structural data: full structural data are available from iucrdata.iucr.org

The title compound, C₁₃H₁₈FNO₅, consists of *D*-fructose with an aromatic amine. The carbohydrate chain is in the acyclic keto form and has the zigzag conformation, while the solid-state NMR data suggests a conformational dimorphism at the aromatic amine group. The carbohydrate portion is involved in extensive O—H···O hydrogen bonding, which forms a two-dimensional network parallel to (001) and organized into fused homodromic ring patterns. The Hirshfeld surface fingerprint plots reveal a major contribution of the non-polar H···H and C···H interactions to the crystal packing forces.



Structure description

The molecular structure and atomic numbering for the title compound (I) are shown in Fig. 1. The molecule is an Amadori rearrangement product (Feather & Mossine, 1998) and can be viewed as a conjugate of a carbohydrate, 1-amino-1-deoxy-*D*-fructose, and an aromatic amine, *N*-methyl-*p*-fluoroaniline, which are joined through the common amino nitrogen atom. The carbohydrate moiety in (I) exists in the acyclic *keto* form. Notably, in the aqueous solution of (I), this tautomeric form is a minor constituent of the equilibrium, at 9.4% of the total population [Supplementary Table 1S; includes references Gomez de Anderez *et al.* (1996) and Mossine *et al.* (2009b)]. The acyclic carbohydrate is in the *zigzag* conformation, having five out of six of its carbon atoms, C2, C3, C4, C5, and C6, located in one plane. The conformation around the carbonyl group is also nearly flat and involves atoms N1, C1, C2, O2, C3, and O3, with the carbonyl O2 atom in a close to a *syn-periplanar* position in respect to both N1 and O3 [respective torsion angles are 8.2 (5) and 9.4 (5)°]. The tertiary amino group geometry is a flattened pyramid, with the distance from the N1 apex to the C1–C7–C13 base of 0.248 (3) Å and the average base–face dihedral angle of 19.3 (4)°. The N1–C7 distance, at 1.409 (4) Å, is significantly shorter

Table 1
Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O3—H3O···O5 ⁱ	0.83 (5)	2.03 (5)	2.782 (4)	151 (4)
O4—H4O···O6 ⁱⁱ	0.94 (6)	1.78 (6)	2.701 (4)	167 (5)
O5—H5O···O3 ⁱⁱⁱ	0.86 (4)	1.84 (4)	2.690 (4)	174 (4)
O6—H6O···O4 ^{iv}	0.86 (5)	2.01 (5)	2.762 (4)	146 (5)

Symmetry codes: (i) $x, y - 1, z$; (ii) $-x + 1, y - \frac{1}{2}, -z + 1$; (iii) $-x, y + \frac{1}{2}, -z + 1$; (iv) $x, y + 1, z$.

Table 2
Suspected O—H···*A* and C—H···*A* contacts (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O3—H3O···O4	0.86 (4)	2.62 (3)	2.940 (3)	103 (3)
O6—H6O···O5	0.86 (5)	2.36 (5)	2.839 (4)	116 (4)
C1—H1A···O2	0.99	2.41	3.299 (5)	149
C3—H3···F1	1.00	2.52	3.432 (5)	151

Symmetry codes: (i) $x, y + 1, z$; (ii) $-x, y + \frac{1}{2}, -z$.

than the distances from N1 to the aliphatic carbon atoms C1 and C13 [1.452 (4) and 1.465 (5) Å], which is an indication for a mixed sp^3/sp^2 hybridization at N1 and a partial resonance of the nitrogen *p*-electrons with the neighboring benzene ring. In the solid-state NMR spectrum of powdered (I) (Fig. 2), the peaks corresponding to C1, C7, C10, and C13 are split at about a 1:2 ratio, indicating the presence of crystals with two different conformations of (I) at the aromatic amine, likely due to configurational inversion at the amino atom N1.

The molecular packing of (I) features alternating ‘carbohydrate’ and ‘hydrocarbon’ layers propagating in the *ab* plane (Fig. 3). The carbohydrate residues form a two-dimensional network of hydrogen bonds (Table 1) organized as a system of two infinite chains, with the ···O3—H···O5—H··· and the ···O4—H···O6—H··· sequences of intermolecular hydrogen bonds. These chains are connected by the intramolecular short heteroatom contacts O3—H···O4 and O6—H···O5. Basic hydrogen-bonding patterns of the resulting network are depicted in Fig. 4 and include fused homodromic rings. In addition, there are close C—H···*A* contacts within the ‘hydrocarbon’ layer that may qualify as weak hydrogen bonds (Table 2). The Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) revealed that a major proportion of the intermolecular contacts in crystal structure of (I) is provided by

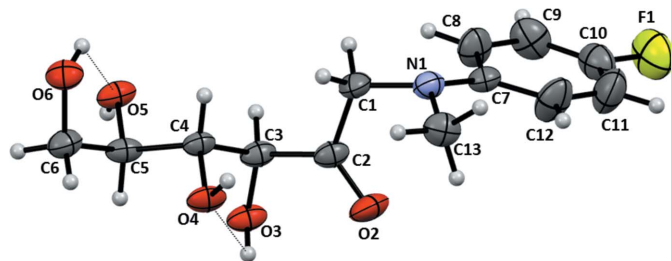


Figure 1
Atomic numbering and displacement ellipsoids at the 50% probability level for (I). Weakly directional intramolecular O—H···O contacts are shown as dotted lines.

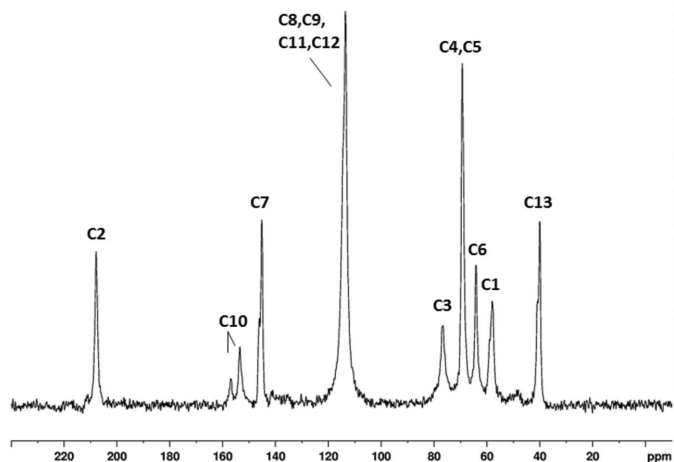


Figure 2
Solid-state ¹³C NMR spectrum of powdered (I).

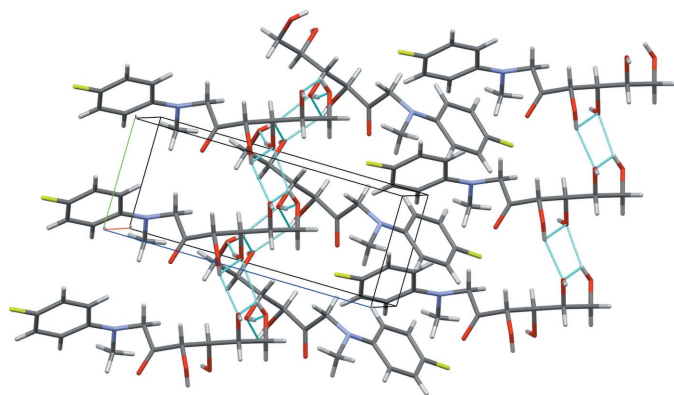


Figure 3
The molecular packing in (I). Color code for crystallographic axes: red – *a*, green – *b*, blue – *c*. Hydrogen bonds are shown as cyan dotted lines.

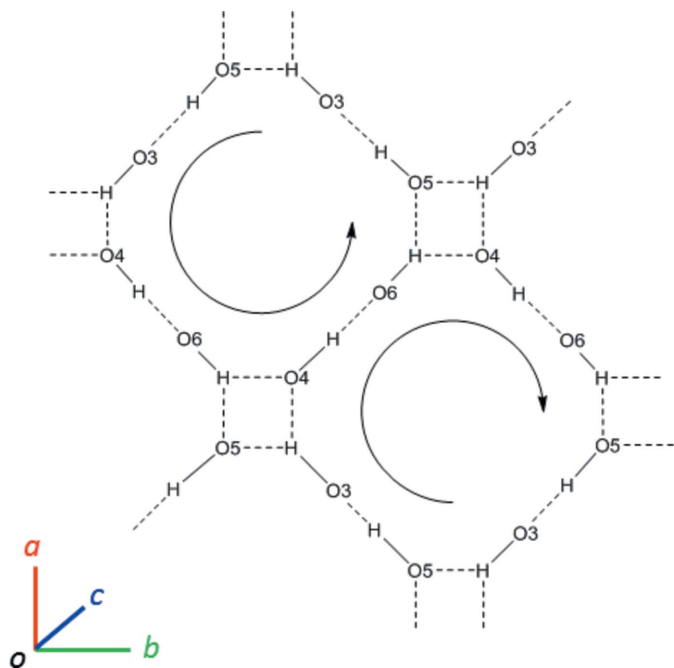


Figure 4
Hydrogen-bonding pattern in the crystal structure of (I).

Table 3Contributions (%) of specific contact types to the Hirshfeld surfaces of (I) and other *N,N*-alkylaryl derivatives of D-fructosamine.

Compound	Alkyl, aryl	O...H	H...H	C...H	Other contacts
(I)	methyl, <i>p</i> -fluorophenyl	26.3	44.6	13.5	F...H 10.9; F...O 2.6; N...H 1.8; C...C 0.3
FruNMpti ^a	methyl, <i>p</i> -methylphenyl	26.5	59.8	11.8	N...H 1.6; C...C 0.3
FruNMPas ^b	methyl, <i>p</i> -methoxyphenyl	32.3	58.2	13.2	N...H 1.6; C...C 0.1
FruNEpca ^a	ethyl, <i>p</i> -chlorophenyl	23.1	50.1	8.6	Cl...H 13.1; Cl...C 3.4; N...C 0.5; C...C 1.3
FruNAlia ^c	allyl, phenyl	15.2	67.7	16.9	C...C 0.1

References: (a) Mossine *et al.* (2009); (b) Mossine *et al.* (2018); (c) Mossine *et al.* (2009a).

non- or low-polar interactions of the H...H and C...H type (Fig. 5 and Table 3).

Synthesis and crystallization

The preparation of (I) has been described previously (Mossine *et al.*, 2009). Briefly, a mixture of 0.02 moles of D-glucose, 0.022 moles of *N*-methyl-*p*-fluoroaniline and 0.55 ml of acetic acid catalyst was stirred for 6 h in 8 ml of 2-propanol at 360 K. The purification step included ion-exchange on Amberlite IRN-77 (H⁺), with 0.2 M NH₄OH in 50% ethanol as an eluant, and was followed by flash filtration on a short silica column using 5% MeOH in CH₂Cl₂ as an eluant. Crystals suitable for the diffraction study were obtained from saturated solution of (I) in water/methanol (1:4) following addition a few drops of acetone at 277 K. See Fig. 2 for the solid-state NMR spectrum of (I).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. As a result of the unrealistic value

obtained for the Flack absolute structure parameter [0.2 (10) for 474 quotients; Parsons *et al.*, 2013], the absolute configuration of the chain system (*3S,4R,5R*) was assigned on the basis of the known configuration for starting D-glucose (McNaught, 1996).

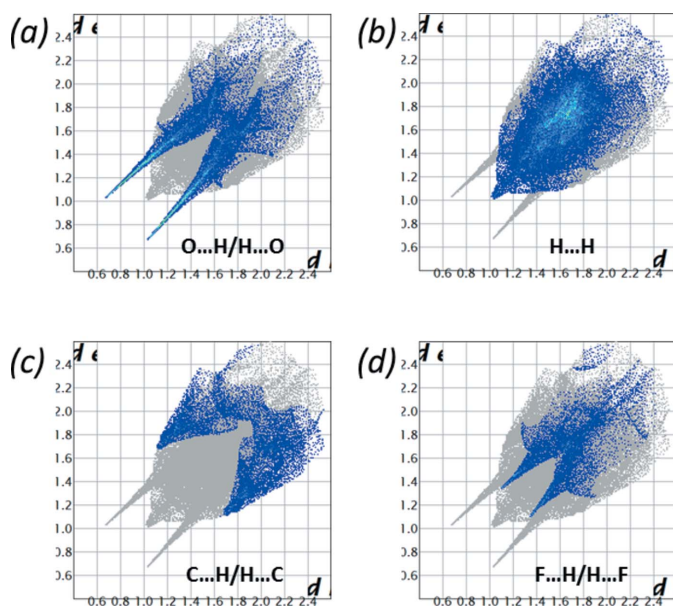
Funding information

Funding for this research was provided by: University of Missouri Agriculture Experiment Station Chemical Laboratories; National Institute of Food and Agriculture (grant No. MO-HABC0002).

Table 4

Experimental details.

Crystal data	
Chemical formula	C ₁₃ H ₁₈ FNO ₅
<i>M_r</i>	287.28
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.561 (6), 5.156 (3), 12.504 (7)
β (°)	90.606 (9)
<i>V</i> (Å ³)	680.9 (6)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.12
Crystal size (mm)	0.50 × 0.10 × 0.05
Data collection	
Diffractometer	Bruker APEXII CCD area detector
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 2003)
<i>T_{min}</i> , <i>T_{max}</i>	0.79, 0.99
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	4693, 2652, 1588
<i>R_{int}</i>	0.039
(sin θ/λ) _{max} (Å ⁻¹)	0.643
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.042, 0.100, 0.95
No. of reflections	2652
No. of parameters	198
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.18, -0.17
Absolute structure	Flack <i>x</i> determined using 474 quotients [(<i>I</i> ⁺) - (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.2 (10)

**Figure 5**

Two-dimensional fingerprint plots produced for the Hirshfeld surface of (I). Contributions to the plots from the O...H, H...H, C...H, and F...H contacts are shown in (a), (b), (c) and (d), respectively.

Computer programs: *SMART* and *SAINT* (Bruker, 1998), *SHELXS97* (Sheldrick, 2008), *SHELXL2017* (Sheldrick, 2015), *X-SEED* (Barbour, 2001), *Mercury* (Macrae *et al.*, 2008), *CIFTAB* (Sheldrick, 2008) and *pubCIF* (Westrip, 2010).

References

- Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
- Bruker. (1998). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Feather, M. S. & Mossine, V. V. (1998). In *The Maillard Reaction in Foods and Medicine*, edited by J. O'Brien, H. E. Nursten and M. J. Crabbe, pp. 37–42. The Royal Society of Chemistry.
- Gomez de Anderez, D., Gil, H., Helliwell, M. & Mata Segreda, J. (1996). *Acta Cryst.* **C52**, 252–254.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- McNaught, A. D. (1996). *Pure Appl. Chem.* **68**, 1919–2008.
- Mossine, V. V., Barnes, C. L., Chance, D. L. & Mawhinney, T. P. (2009). *Angew. Chem. Int. Ed.* **48**, 5517–5520.
- Mossine, V. V., Barnes, C. L. & Mawhinney, T. P. (2009a). *Carbohydr. Res.* **344**, 948–951.
- Mossine, V. V., Barnes, C. L. & Mawhinney, T. P. (2009b). *J. Carbohydr. Chem.* **28**, 245–263.
- Mossine, V. V., Barnes, C. L. & Mawhinney, T. P. (2018). *Acta Cryst.* **E74**, 127–132.
- Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* **B69**, 249–259.
- Sheldrick, G. M. (2003). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

full crystallographic data

IUCrData (2018). 3, x180369 [https://doi.org/10.1107/S2414314618003693]

1-Deoxy-1-(*N*-methyl-4-fluorophenylamino)-*D*-arabino-hexulose

Valeri V. Mossine, Charles L. Barnes and Thomas P. Mawhinney

1-Deoxy-1-(*N*-methyl-4-fluorophenylamino)-*D*-arabino-hexulose*Crystal data*

$C_{13}H_{18}FNO_5$	$F(000) = 304$
$M_r = 287.28$	$D_x = 1.401 \text{ Mg m}^{-3}$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 10.561 (6) \text{ \AA}$	Cell parameters from 1387 reflections
$b = 5.156 (3) \text{ \AA}$	$\theta = 2.5\text{--}24.4^\circ$
$c = 12.504 (7) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$\beta = 90.606 (9)^\circ$	$T = 100 \text{ K}$
$V = 680.9 (6) \text{ \AA}^3$	Needle, colourless
$Z = 2$	$0.50 \times 0.10 \times 0.05 \text{ mm}$

Data collection

Bruker APEXII CCD area detector diffractometer	2652 independent reflections
ω scans	1588 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$R_{\text{int}} = 0.039$
$T_{\text{min}} = 0.79$, $T_{\text{max}} = 0.99$	$\theta_{\text{max}} = 27.2^\circ$, $\theta_{\text{min}} = 1.6^\circ$
4693 measured reflections	$h = -13 \rightarrow 13$
	$k = -6 \rightarrow 6$
	$l = -15 \rightarrow 14$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.100$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.95$	$\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
2652 reflections	$\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$
198 parameters	Absolute structure: Flack x determined using
1 restraint	474 quotients $[(I^-)-(I)]/[(I^+)+(I)]$ (Parsons <i>et al.</i> , 2013)
Hydrogen site location: mixed	Absolute structure parameter: 0.2 (10)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Hydroxy and nitrogen-bound H-atoms were located in difference-Fourier analyses and were allowed to refine fully. Other H atoms were placed at calculated positions and treated as riding, with C—H = 0.98 Å (methyl), 0.99 Å (methylene) or 1.00 Å (methine) and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{methine or methylene})$ or $1.5U_{\text{eq}}(\text{methyl})$.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
F1	0.0320 (2)	0.1152 (6)	−0.2413 (2)	0.0782 (9)
N1	0.3656 (3)	0.1754 (6)	0.1042 (2)	0.0343 (8)
C1	0.3239 (4)	0.2826 (7)	0.2053 (3)	0.0374 (10)
H1A	0.277228	0.445581	0.190761	0.045*
H1B	0.399564	0.327236	0.248943	0.045*
O2	0.2218 (2)	−0.1203 (5)	0.2449 (2)	0.0472 (8)
C2	0.2394 (3)	0.1037 (8)	0.2706 (3)	0.0329 (9)
O3	0.0910 (2)	0.0429 (5)	0.4150 (2)	0.0375 (7)
C3	0.1810 (3)	0.2174 (7)	0.3703 (3)	0.0323 (10)
H3	0.135141	0.379624	0.349283	0.039*
O4	0.3611 (2)	0.0655 (5)	0.4743 (2)	0.0364 (7)
C4	0.2844 (3)	0.2909 (7)	0.4525 (3)	0.0289 (9)
H4	0.338661	0.431473	0.422352	0.035*
O5	0.1544 (2)	0.6087 (5)	0.5363 (2)	0.0360 (7)
C5	0.2283 (3)	0.3818 (8)	0.5579 (3)	0.0323 (9)
H5	0.171498	0.242944	0.585874	0.039*
O6	0.4085 (2)	0.6539 (5)	0.6102 (2)	0.0387 (7)
C6	0.3272 (3)	0.4450 (7)	0.6423 (3)	0.0383 (10)
H6A	0.284356	0.493149	0.709461	0.046*
H6B	0.379111	0.288784	0.656630	0.046*
C7	0.2775 (3)	0.1567 (7)	0.0191 (3)	0.0318 (8)
C8	0.1716 (4)	0.3148 (9)	0.0110 (3)	0.0479 (11)
H8	0.155226	0.435436	0.066554	0.058*
C9	0.0895 (4)	0.3024 (10)	−0.0752 (4)	0.0551 (12)
H9	0.017345	0.412140	−0.078552	0.066*
C10	0.1128 (4)	0.1321 (9)	−0.1549 (3)	0.0511 (12)
C11	0.2163 (5)	−0.0204 (10)	−0.1523 (4)	0.0669 (14)
H11	0.232965	−0.135503	−0.209800	0.080*
C12	0.2978 (4)	−0.0084 (9)	−0.0658 (3)	0.0605 (14)
H12	0.370320	−0.117390	−0.064489	0.073*
C13	0.4626 (3)	−0.0266 (8)	0.1133 (3)	0.0425 (10)
H13A	0.421826	−0.197004	0.117209	0.064*
H13B	0.513541	0.002372	0.178204	0.064*
H13C	0.517502	−0.020370	0.050643	0.064*
H4O	0.438 (5)	0.077 (13)	0.438 (4)	0.11 (2)*
H5O	0.078 (4)	0.584 (9)	0.556 (3)	0.055 (13)*
H3O	0.129 (4)	−0.090 (10)	0.434 (3)	0.055 (15)*
H6O	0.363 (5)	0.753 (10)	0.570 (4)	0.09 (2)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0717 (17)	0.100 (2)	0.0620 (16)	-0.0097 (17)	-0.0238 (14)	0.0038 (16)
N1	0.0397 (17)	0.0258 (18)	0.0377 (18)	0.0002 (15)	0.0064 (15)	-0.0010 (14)
C1	0.045 (2)	0.026 (2)	0.041 (2)	-0.0094 (18)	0.0030 (19)	-0.0010 (18)
O2	0.0494 (16)	0.0234 (16)	0.069 (2)	-0.0055 (13)	0.0165 (14)	-0.0069 (14)
C2	0.0263 (17)	0.024 (2)	0.049 (2)	0.0029 (16)	0.0035 (16)	0.0002 (18)
O3	0.0253 (14)	0.0256 (16)	0.0617 (19)	-0.0006 (13)	0.0072 (12)	0.0028 (14)
C3	0.0248 (19)	0.024 (2)	0.048 (2)	0.0000 (16)	0.0065 (18)	0.0017 (18)
O4	0.0296 (14)	0.0230 (14)	0.0567 (17)	0.0060 (12)	0.0045 (13)	0.0045 (13)
C4	0.0283 (19)	0.021 (2)	0.038 (2)	0.0018 (16)	0.0031 (18)	0.0015 (17)
O5	0.0238 (14)	0.0235 (15)	0.0610 (18)	0.0018 (12)	0.0113 (12)	0.0009 (13)
C5	0.0238 (19)	0.023 (2)	0.050 (3)	0.0015 (17)	0.0074 (18)	0.0058 (18)
O6	0.0283 (14)	0.0366 (18)	0.0513 (17)	-0.0062 (13)	-0.0005 (13)	0.0044 (14)
C6	0.038 (2)	0.028 (3)	0.048 (3)	-0.0034 (18)	0.007 (2)	0.0000 (19)
C7	0.0326 (19)	0.024 (2)	0.039 (2)	-0.0036 (17)	0.0006 (17)	0.0017 (18)
C8	0.051 (3)	0.046 (3)	0.047 (3)	0.017 (2)	0.003 (2)	-0.009 (2)
C9	0.046 (3)	0.065 (3)	0.055 (3)	0.017 (2)	0.002 (2)	0.005 (3)
C10	0.048 (3)	0.059 (3)	0.046 (3)	-0.008 (2)	-0.011 (2)	0.007 (2)
C11	0.084 (3)	0.059 (3)	0.057 (3)	0.008 (3)	-0.015 (3)	-0.023 (3)
C12	0.065 (3)	0.046 (3)	0.069 (3)	0.024 (2)	-0.018 (3)	-0.019 (3)
C13	0.034 (2)	0.042 (2)	0.051 (3)	0.0066 (19)	0.0051 (19)	0.004 (2)

Geometric parameters (Å, °)

F1—C10	1.373 (4)	C5—C6	1.512 (5)
N1—C7	1.409 (4)	C5—H5	1.0000
N1—C1	1.452 (4)	O6—C6	1.437 (4)
N1—C13	1.465 (5)	O6—H6O	0.86 (5)
C1—C2	1.527 (5)	C6—H6A	0.9900
C1—H1A	0.9900	C6—H6B	0.9900
C1—H1B	0.9900	C7—C12	1.379 (5)
O2—C2	1.213 (4)	C7—C8	1.387 (5)
C2—C3	1.515 (5)	C8—C9	1.377 (5)
O3—C3	1.427 (4)	C8—H8	0.9500
O3—H3O	0.83 (5)	C9—C10	1.353 (6)
C3—C4	1.539 (5)	C9—H9	0.9500
C3—H3	1.0000	C10—C11	1.347 (6)
O4—C4	1.441 (4)	C11—C12	1.377 (6)
O4—H4O	0.94 (6)	C11—H11	0.9500
C4—C5	1.524 (4)	C12—H12	0.9500
C4—H4	1.0000	C13—H13A	0.9800
O5—C5	1.431 (4)	C13—H13B	0.9800
O5—H5O	0.86 (4)	C13—H13C	0.9800
C7—N1—C1	118.7 (3)	C4—C5—H5	108.8
C7—N1—C13	117.8 (3)	C6—O6—H6O	106 (3)

C1—N1—C13	114.9 (3)	O6—C6—C5	112.2 (3)
N1—C1—C2	114.8 (3)	O6—C6—H6A	109.2
N1—C1—H1A	108.6	C5—C6—H6A	109.2
C2—C1—H1A	108.6	O6—C6—H6B	109.2
N1—C1—H1B	108.6	C5—C6—H6B	109.2
C2—C1—H1B	108.6	H6A—C6—H6B	107.9
H1A—C1—H1B	107.5	C12—C7—C8	116.0 (4)
O2—C2—C3	121.6 (3)	C12—C7—N1	121.1 (3)
O2—C2—C1	121.5 (3)	C8—C7—N1	122.7 (3)
C3—C2—C1	116.9 (3)	C9—C8—C7	122.0 (4)
C3—O3—H3O	108 (3)	C9—C8—H8	119.0
O3—C3—C2	110.9 (3)	C7—C8—H8	119.0
O3—C3—C4	111.4 (3)	C10—C9—C8	119.3 (4)
C2—C3—C4	110.6 (3)	C10—C9—H9	120.4
O3—C3—H3	107.9	C8—C9—H9	120.4
C2—C3—H3	107.9	C11—C10—C9	121.0 (4)
C4—C3—H3	107.9	C11—C10—F1	118.7 (4)
C4—O4—H4O	110 (4)	C9—C10—F1	120.3 (4)
O4—C4—C5	107.9 (3)	C10—C11—C12	119.5 (4)
O4—C4—C3	108.7 (3)	C10—C11—H11	120.2
C5—C4—C3	111.9 (3)	C12—C11—H11	120.2
O4—C4—H4	109.4	C11—C12—C7	122.1 (4)
C5—C4—H4	109.4	C11—C12—H12	118.9
C3—C4—H4	109.4	C7—C12—H12	118.9
C5—O5—H5O	110 (3)	N1—C13—H13A	109.5
O5—C5—C6	109.1 (3)	N1—C13—H13B	109.5
O5—C5—C4	107.7 (3)	H13A—C13—H13B	109.5
C6—C5—C4	113.5 (3)	N1—C13—H13C	109.5
O5—C5—H5	108.8	H13A—C13—H13C	109.5
C6—C5—H5	108.8	H13B—C13—H13C	109.5
C7—N1—C1—C2	73.7 (4)	O5—C5—C6—O6	-58.2 (4)
C13—N1—C1—C2	-73.4 (4)	C4—C5—C6—O6	61.9 (4)
N1—C1—C2—O2	8.2 (5)	C1—N1—C7—C12	-160.5 (4)
N1—C1—C2—C3	-173.1 (3)	C13—N1—C7—C12	-14.3 (5)
O2—C2—C3—O3	-9.4 (5)	C1—N1—C7—C8	24.7 (5)
C1—C2—C3—O3	171.8 (3)	C13—N1—C7—C8	170.8 (4)
O2—C2—C3—C4	114.7 (4)	C12—C7—C8—C9	1.9 (6)
C1—C2—C3—C4	-64.0 (4)	N1—C7—C8—C9	177.0 (4)
O3—C3—C4—O4	68.4 (4)	C7—C8—C9—C10	-0.4 (7)
C2—C3—C4—O4	-55.4 (4)	C8—C9—C10—C11	-1.6 (7)
O3—C3—C4—C5	-50.7 (4)	C8—C9—C10—F1	179.7 (4)
C2—C3—C4—C5	-174.5 (3)	C9—C10—C11—C12	1.9 (7)
O4—C4—C5—O5	178.8 (3)	F1—C10—C11—C12	-179.3 (4)
C3—C4—C5—O5	-61.6 (3)	C10—C11—C12—C7	-0.3 (7)
O4—C4—C5—C6	58.0 (4)	C8—C7—C12—C11	-1.5 (6)
C3—C4—C5—C6	177.6 (3)	N1—C7—C12—C11	-176.7 (4)

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3O \cdots O5 ⁱ	0.83 (5)	2.03 (5)	2.782 (4)	151 (4)
O4—H4O \cdots O6 ⁱⁱ	0.94 (6)	1.78 (6)	2.701 (4)	167 (5)
O5—H5O \cdots O3 ⁱⁱⁱ	0.86 (4)	1.84 (4)	2.690 (4)	174 (4)
O6—H6O \cdots O4 ^{iv}	0.86 (5)	2.01 (5)	2.762 (4)	146 (5)

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+1, y-1/2, -z+1$; (iii) $-x, y+1/2, -z+1$; (iv) $x, y+1, z$.

Supplementary Table 1S. Distribution (%) of cyclic and acyclic forms of some 1-amino-1-deoxy-D-fructose derivatives in D2O/pyridine (1:1) at 293 K, as estimated from the ¹³C NMR spectra, and in the crystalline state

Compound	Amine substituents						Crystalline isomers
		α -pyranose	β -pyranose	α -furanose	β -furanose	acyclic, keto	
(I) [a]	methyl, <i>p</i> -fluorophenyl	2.5	52.1	5.0	31.0	9.4	acyclic keto
FruNMpti ^a	methyl, <i>p</i> -methylphenyl	2.1	49.9	4.8	32.2	11.0	acyclic keto
FruNMPas ^b	methyl, <i>p</i> -methoxyphenyl	2.1	52.0	4.9	30.6	10.3	acyclic keto
FruNEpca ^a	ethyl, <i>p</i> -chlorophenyl	2.0	48.7	4.2	32.3	12.7	acyclic keto
Frupti ^{a,c}	H, phenyl	3.5	61.0	9.4	24.2	1.9	β -pyranose
FruNAla ^d	allyl, phenyl	2.2	47.4	4.5	33.6	12.3	β -pyranose
Fructosamine ^e	none	5.0	70.8	11.2	12.3	0.8	β -pyranose

References: (a) Mossine *et al.* (2009); (b) Mossine *et al.* (2018); (c) Gomez de Anderez *et al.* (1996); (d) Mossine *et al.* (2009a); (e) Mossine *et al.* (2009b).