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N-(*p*-Tolyl)-*β*-L-rhamnopyranosylamine 1.5-hydrate

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The title rhamnopyranosylamine, $C_{13}H_{19}NO_4\cdot1.5H_2O$, was isolated as an intermediate in the Amadori rearrangement of L-rhamnose with *p*-toluidine. Two independent molecules and three water molecules of crystallization comprise the asymmetric unit, and these components are held together *via* extensive hydrogen-bonding interactions.

Key indicators

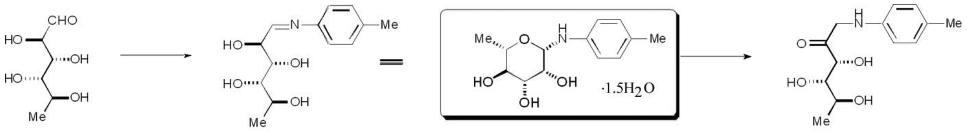
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
Disorder in main residue
R factor = 0.036
wR factor = 0.096
Data-to-parameter ratio = 12.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The major non-enzymatic conjugation of proteins with carbohydrates occurs by the Amadori rearrangement (Amadori, 1925; Hodge, 1955). Further chemistry of the Amadori products, *in vivo*, leads to advanced glycation end-products (AGEs; Lapolla *et al.*, 2005). AGEs are a heterogeneous group of compounds, which accumulate in plasma and tissues, and are implicated in late onset diabetes (Smit & Lutgers, 2004) and amyloid pathologies (Horvat & Jakas, 2004). At higher temperatures, the Amadori rearrangement is the first step in the Maillard reaction, the products of which are responsible for much of the flavour and colour generated during baking and roasting (Martins & Van Boekel, 2005; Kwak & Lim, 2004; Mottram *et al.*, 2002).

Studies of the Amadori reaction of L-rhamnose, (1), with primary and secondary amines are in progress. Recently, the crystal structure of the product, (4), of the Amadori reaction between L-rhamnose and dibenzylamine has been reported (Harding *et al.*, 2005). In the reaction between (1) and *p*-toluidine in acetic acid, to give the ketosamine, (4), the initial product, (2), was isolated as an intermediate (Funcke, 1978). The solution NMR of (2) is complex and indicates a mixture of forms; the formation of crystals allowed the unambiguous identification of the *β*-pyranosylamine, (3), as an early intermediate involved in the reaction.



(1) (2) (3) (4)

The title compound, (3), crystallizes with two molecules in the asymmetric unit, as well as three water molecules of crystallization (Fig. 1 and Table 1). An evident pseudo-translational symmetry exists, in which the pyranose rings are mostly superimposable while the aromatic rings are slightly tilted. This is shown by the torsion angle being 172.00 (15)° for C1—N11—C12—C13 in one molecule and 153.87 (15)° for C101—N111—C112—C113 in the other.

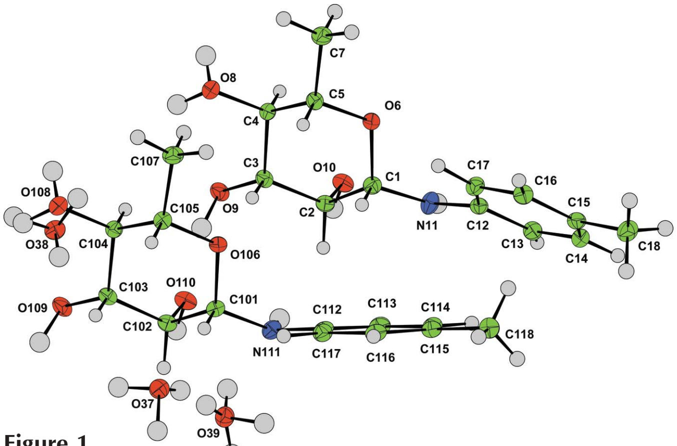


Figure 1
The asymmetric unit of (3), with displacement ellipsoids drawn at the 50% probability level. H-atom radii are arbitrary. The difference density synthesis suggested the presence of two H atoms bonded to O8 on one molecule and O108 on the other, each with 50% site occupancy. Atoms O37 and O38 carry three H atoms with 33% site occupancy. Atom O39 carries four H atoms with 25% site occupancy. This abnormal water molecule geometry is needed to explain the complex hydrogen-bond network (see *Comment*).

No symmetry can be seen in the position of the three solvent molecules. The final refinement suggested the presence of two H atoms bonded to a hydroxy O atom, namely atom O_8 on one molecule and O_{108} on the other, each with 50% site occupancy. In addition, two molecules of water, *viz.* O_{37} and O_{38}, carry three H atoms (one H atom with full occupancy and the other two with 50% occupancy) and the remaining water molecules carries four H atoms (each with 50% occupancy). The occupancies of these H atoms were all set on the basis of symmetry and steric effects. The structure shows a complicated hydrogen-bonded network (Fig. 2 and Table 2). This latter feature is mainly a result of interactions between molecules of the title compound, between molecules of the title compound and water, and among the water molecules themselves. The basic building block of the structure can be thought of as a dimer in which two molecules of the title compound are held together by the strong hydrogen bonds O9—H91···O110 and O109—H1091···O10$^{\rm iii}$ (symmetry code as in Table 2).

Experimental

The title material was crystallized by dissolving it in methanol and allowing the slow evaporation of the solvent until pale-orange crystals formed.

Crystal data

$C_{13}H_{19}NO_4\cdot1.5H_2O$
$M_r = 280.32$
Orthorhombic, $P2_12_12_1$
$a = 8.0521$ (1) Å
$b = 9.7110$ (1) Å
$c = 35.8868$ (4) Å
$V = 2806.13$ (6) Å^3
$Z = 8$
$D_x = 1.327$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 4116 reflections
$\theta = 5$–$30°$
$\mu = 0.10$ mm^{-1}
$T = 100$ K
Block, orange
0.45 × 0.30 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\rm min} = 0.96$, $T_{\rm max} = 0.98$
7406 measured reflections

4232 independent reflections
3788 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.013$
$\theta_{\rm max} = 29.1°$
$h = -10 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -48 \rightarrow 49$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.096$
$S = 0.95$
4232 reflections
352 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + 0.06 + 0.37P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.28$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.30$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.529 (2)	C101—C102	1.535 (2)
C1—O6	1.4476 (18)	C101—O106	1.4477 (19)
C1—N11	1.413 (2)	C101—N111	1.424 (2)
C2—C3	1.528 (2)	C102—C103	1.522 (2)
C2—O10	1.4295 (19)	C102—O110	1.4373 (19)
C3—C4	1.518 (2)	C103—C104	1.521 (2)
C3—O9	1.4372 (18)	C103—O109	1.4349 (18)
C4—C5	1.533 (2)	C104—C105	1.538 (2)
C4—O8	1.4269 (19)	C104—O108	1.4303 (19)
C5—O6	1.4311 (19)	C105—O106	1.4351 (19)
C5—C7	1.512 (2)	C105—C107	1.514 (2)
N11—C12	1.401 (2)	N111—C112	1.408 (2)
C12—C13	1.394 (2)	C112—C117	1.395 (2)
C12—C17	1.397 (2)	C112—C113	1.398 (2)
C13—C14	1.392 (2)	C117—C116	1.393 (2)
C14—C15	1.393 (2)	C116—C115	1.395 (2)
C15—C16	1.390 (2)	C115—C114	1.395 (2)
C15—C18	1.507 (2)	C115—C118	1.509 (2)
C16—C17	1.390 (2)	C114—C113	1.387 (2)
C2—C1—O6	110.54 (12)	C102—C101—O106	109.99 (12)
C2—C1—N11	110.51 (13)	C102—C101—N111	109.26 (13)
O6—C1—N11	109.40 (13)	O106—C101—N111	110.04 (13)
C1—C2—C3	109.33 (13)	C101—C102—C103	109.14 (13)
C1—C2—O10	109.69 (13)	C101—C102—O110	109.35 (13)
C3—C2—O10	112.30 (12)	C103—C102—O110	111.85 (13)
C2—C3—C4	110.65 (12)	C102—C103—C104	110.81 (13)
C2—C3—O9	110.77 (13)	C102—C103—O109	110.89 (13)
C4—C3—O9	109.89 (12)	C104—C103—O109	109.61 (13)
C3—C4—C5	107.49 (12)	C103—C104—C105	107.62 (12)
C3—C4—O8	109.94 (12)	C103—C104—O108	109.47 (12)
C5—C4—O8	110.20 (13)	C105—C104—O108	109.90 (13)
C4—C5—O6	107.93 (12)	C104—C105—O106	108.67 (12)
C4—C5—C7	114.03 (13)	C104—C105—C107	112.91 (13)
O6—C5—C7	107.52 (12)	O106—C105—C107	107.79 (13)
C1—O6—C5	112.16 (12)	C101—O106—C105	112.69 (12)
C1—N11—C12	122.72 (13)	C101—N111—C112	123.04 (13)
N11—C12—C13	119.39 (14)	N111—C112—C117	122.81 (14)
N11—C12—C17	121.78 (14)	N111—C112—C113	118.84 (14)
C13—C12—C17	118.80 (14)	C117—C112—C113	118.27 (15)
C12—C13—C14	120.25 (15)	C112—C117—C116	120.02 (15)
C13—C14—C15	121.48 (15)	C117—C116—C115	122.10 (15)
C14—C15—C16	117.58 (15)	C116—C115—C114	117.25 (15)
C14—C15—C18	121.11 (15)	C116—C115—C118	121.96 (15)
C16—C15—C18	121.30 (15)	C114—C115—C118	120.79 (15)
C15—C16—C17	121.81 (15)	C115—C114—C113	121.27 (15)
C12—C17—C16	119.99 (15)	C112—C113—C114	121.07 (15)

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Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O37—H372···O9^{i}	0.93	1.87	2.8000 (16)	175
O9—H91···O110	0.97	1.92	2.8610 (16)	164
O10—H101···O38^{ii}	0.93	1.81	2.7162 (16)	167
O109—H1091···O10^{iii}	0.98	1.88	2.8141 (17)	159
O38—H381···O109	0.93	1.83	2.7648 (16)	176
O110—H1101···O37	0.98	1.75	2.7273 (16)	172
O8—H82···O39^{iv}	0.96	1.84	2.7531 (16)	161
O37—H373···O108^{v}	0.98	1.86	2.7941 (16)	159
O108—H1082···O39^{i}	1.02	1.86	2.8115 (16)	154
O108—H1081···O37^{iv}	0.79	2.02	2.7941 (16)	166
O8—H81···O38^{vi}	0.77	2.02	2.7795 (16)	167
O38—H382···O8^{vii}	0.98	1.82	2.7795 (16)	166
O39—H392···O108^{ii}	0.81	2.08	2.8115 (16)	150
O37—H371···O39	0.92	1.94	2.8378 (17)	164
O39—H391···O8^{v}	0.89	2.03	2.7531 (16)	138
O39—H393···O37	0.81	2.04	2.8378 (17)	171
O38—H383···O39^{iv}	0.88	1.99	2.8313 (17)	159
O39—H394···O38^{v}	0.95	2.09	2.8313 (17)	134

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x, y-1, z$; (iv) $x-1, y, z$; (v) $x+1, y, z$; (vi) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$; (vii) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$.

H atoms were located in difference maps. Those attached to C atoms were repositioned geometrically, while those associated with water molecules were located in the difference map during subsequent cycles of least-squares. H atoms were initially refined with soft restraints on the bonds to regularize their geometry (C—H = 0.97–1.00 Å, N—H = 0.93 Å and O—H = 0.77–1.02 Å), after which they were refined in the riding-model approximation, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N) for those bonded to C or N atoms, and $U_{\rm iso}$(H) = 0.05 Å^2 for those bonded to O atoms.

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

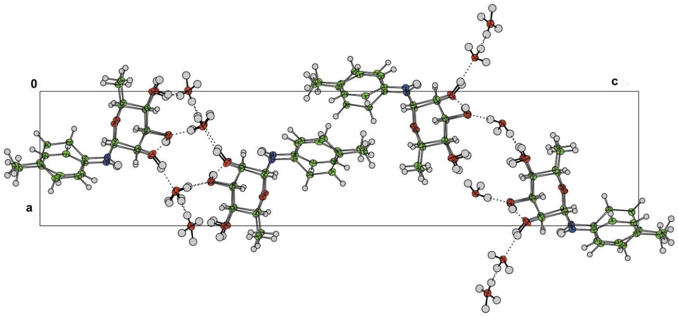

Figure 2
Packing diagram of (3), viewed down the b axis. Hydrogen bonds are shown as dashed lines.

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