Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

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

Francesco Punzo,[a]*‡ David J. Watkin,[b] Joseph M. D. Cook,[c] David Hotchkiss[c] and George W. J. Fleet[c]

[a]Dipartimento di Scienze Chimiche, Facoltà di Farmacia, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy, [b]Department of Chemical Crystallography, Chemical Research Laboratory, Mansfield Road, Oxford OX1 3TA, England, and [c]Department of Organic Chemistry, Chemical Research Laboratory, University of Oxford, Mansfield Road, Oxford OX1 3TA, England

‡ Visiting scientist at the Department of Chemical Crystallography, Chemical Research Laboratory, University of Oxford, Mansfield Road, Oxford OX1 3TA, England.

Correspondence e-mail: fpunzo@unict.it

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.

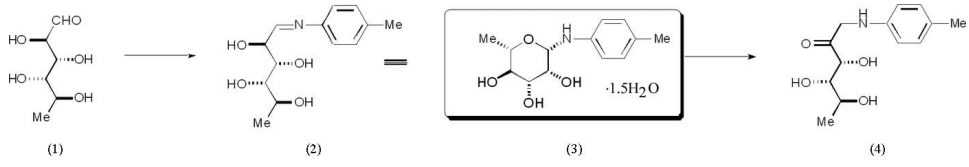
Received 26 May 2005
Accepted 10 June 2005
Online 17 June 2005

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.

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.



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.

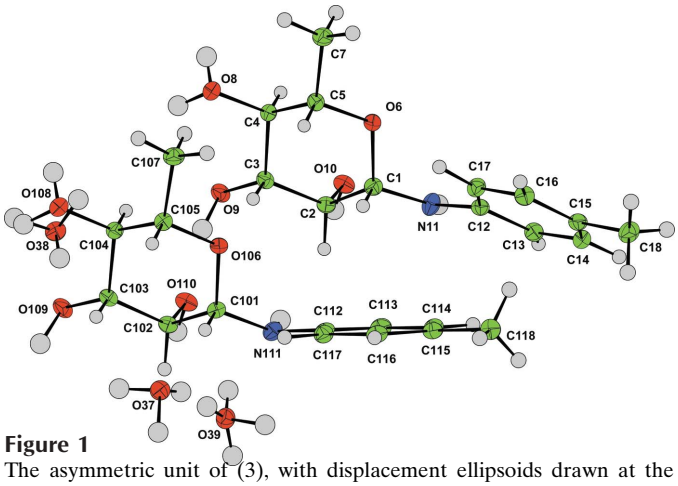


Figure 1
The asymmetric unit of (3), with displacement ellipsoids drawn at the 50% probability level. H-atom radii are arbitrary. The difference density synthesis suggested the presence of two H atoms bonded to O8 on one molecule and O108 on the other, each with 50% site occupancy. Atoms O37 and O38 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^{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

$C_{13}H_{19}NO_4{\cdot}1.5H_2O$
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
θ = 5–30°
μ = 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_{min} = 0.96, T_{max} = 0.98
7406 measured reflections
4232 independent reflections
3788 reflections with $I > 2\sigma(I)$
R_{int} = 0.013
θ_{max} = 29.1°
h = −10 → 11
k = −13 → 13
l = −48 → 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
$w = 1/[\sigma^2(F^2) + 0.06 + 0.37P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −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)

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_{iso}(H) = 1.2U_{eq}(C,N) for those bonded to C or N atoms, and U_{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*.

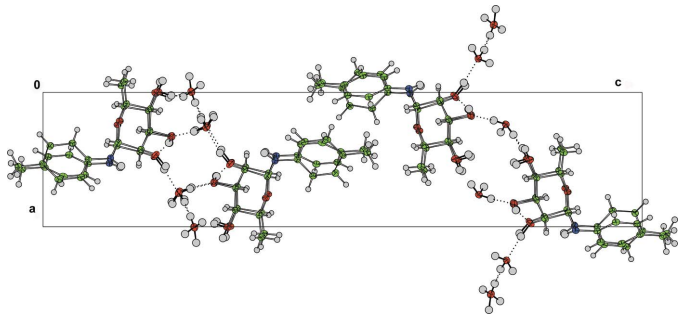


Figure 2
Packing diagram of (3), viewed down the *b* axis. Hydrogen bonds are shown as dashed lines.

References

Altomare, A., Cascarano, G., Giacovazzo, G., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Amadori, M. (1925). *Atti Accad. Naz. Lincei*, **2**, 337–345.
Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
Funcke, W. (1978). *Justus Liebigs Ann. Chem.* **12**, 2009–2104.
Harding, C. C., Watkin, D. J., Hotchkiss, D. J., Cook, J. M. D. & Fleet, G. W. J. (2005). *Acta Cryst.* E**61**, o995–o997.
Hodge, J. E. (1955). *Adv. Carbohydr. Chem.* **10**, 169–205.
Horvat, S. & Jakas, A. (2004). *J. Pept. Sci.* **10**, 119–137.
Kwak, E. J. & Lim, S. I. (2004). *Amino Acids*, **27**, 85–90.
Lapolla, A., Traldi, P. & Fedele, D. (2005). *Clin. Biochem.* **38**, 103–115.
Martins, S. I. F. S. & Van Boekel, M. A. J. S. (2005). *Food Chem.* **90**, 257–269.
Mottram, D. S., Wedzicha, B. L. & Dodson, A. T. (2002). *Nature* (*London*), **419**, 448–449.
Nonius (2001). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Smit, A. J. & Lutgers, H. L. (2004). *Curr. Med. Chem.* **11**, 2767–2784.
Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.

supporting information

Acta Cryst. (2005). E**61**, o2155–o2157 [https://doi.org/10.1107/S1600536805018489]

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

Francesco Punzo, David J. Watkin, Joseph M. D. Cook, David Hotchkiss and George W. J. Fleet

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

Crystal data

$C_{13}H_{19}NO_4 \cdot 1.5H_2O$
$M_r = 280.32$
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
$Z = 8$
$F(000) = 1208$
$D_x = 1.327$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
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
Graphite monochromator
ω scans
Absorption correction: multi-scan (DENZO/SCALEPACK; Otwinowski & Minor, 1997)
$T_{min} = 0.96$, $T_{max} = 0.98$
7406 measured reflections
4232 independent reflections
3788 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$
$\theta_{max} = 29.1°$, $\theta_{min} = 5.2°$
$h = -10 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -48 \rightarrow 49$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.096$
$S = 0.95$
4232 reflections
352 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F^2) + 0.06 + 0.37P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.37332 (19)	0.91878 (17)	0.87439 (4)	0.0169	
C2	0.42518 (19)	0.86119 (16)	0.83647 (4)	0.0161	
C3	0.2871 (2)	0.76877 (17)	0.82141 (4)	0.0159	
C4	0.12283 (19)	0.84542 (16)	0.82062 (4)	0.0151	
C5	0.08494 (19)	0.89192 (17)	0.86056 (4)	0.0161	

O6	0.21286 (13)	0.98535 (12)	0.87184 (3)	0.0170
C7	−0.0794 (2)	0.96569 (19)	0.86478 (5)	0.0210
O8	−0.00548 (15)	0.75670 (12)	0.80737 (3)	0.0199
O9	0.32720 (15)	0.72002 (12)	0.78468 (3)	0.0194
O10	0.46352 (14)	0.97201 (12)	0.81171 (3)	0.0186
N11	0.49213 (17)	1.01430 (15)	0.88745 (4)	0.0205
C12	0.49970 (19)	1.05700 (16)	0.92470 (4)	0.0164
C13	0.6326 (2)	1.13788 (17)	0.93652 (5)	0.0187
C14	0.6484 (2)	1.17349 (17)	0.97393 (5)	0.0199
C15	0.5333 (2)	1.12999 (17)	1.00043 (4)	0.0186
C16	0.3990 (2)	1.05259 (17)	0.98804 (4)	0.0195
C17	0.3797 (2)	1.01758 (17)	0.95072 (4)	0.0190
C18	0.5551 (2)	1.1642 (2)	1.04110 (5)	0.0241
C101	0.39909 (19)	0.41598 (17)	0.87693 (4)	0.0164
C102	0.4424 (2)	0.36105 (17)	0.83801 (4)	0.0168
C103	0.2995 (2)	0.27287 (17)	0.82383 (4)	0.0165
C104	0.13748 (19)	0.35352 (17)	0.82426 (4)	0.0158
C105	0.1068 (2)	0.40134 (17)	0.86455 (4)	0.0164
O106	0.24190 (13)	0.48823 (12)	0.87581 (3)	0.0166
C107	−0.0523 (2)	0.48288 (19)	0.86882 (5)	0.0209
O108	0.00461 (15)	0.26632 (12)	0.81230 (3)	0.0207
O109	0.33204 (16)	0.22422 (13)	0.78679 (3)	0.0210
O110	0.47634 (14)	0.47484 (12)	0.81356 (3)	0.0192
N111	0.52717 (17)	0.50647 (15)	0.88914 (4)	0.0191
C112	0.53241 (19)	0.56291 (16)	0.92526 (4)	0.0172
C117	0.4662 (2)	0.49596 (17)	0.95628 (4)	0.0192
C116	0.4790 (2)	0.55581 (17)	0.99145 (5)	0.0196
C115	0.5575 (2)	0.68222 (17)	0.99707 (5)	0.0200
C114	0.6260 (2)	0.74664 (17)	0.96591 (5)	0.0206
C113	0.6144 (2)	0.68817 (18)	0.93073 (5)	0.0209
C118	0.5678 (2)	0.74828 (18)	1.03505 (5)	0.0233
O37	0.75028 (14)	0.40028 (13)	0.77368 (3)	0.0204
O38	0.26271 (14)	0.39716 (12)	0.72760 (3)	0.0200
O39	1.00308 (15)	0.57948 (14)	0.74752 (3)	0.0211
H11	0.3623	0.8416	0.8918	0.0215*
H21	0.5270	0.8059	0.8399	0.0208*
H31	0.2728	0.6885	0.8384	0.0206*
H41	0.1314	0.9264	0.8040	0.0205*
H51	0.0853	0.8089	0.8769	0.0199*
H71	−0.0971	0.9903	0.8908	0.0271*
H72	−0.1740	0.9060	0.8570	0.0271*
H73	−0.0823	1.0499	0.8498	0.0271*
H131	0.7140	1.1722	0.9184	0.0230*
H141	0.7420	1.2302	0.9817	0.0243*
H161	0.3131	1.0219	1.0058	0.0243*
H171	0.2793	0.9648	0.9427	0.0239*
H181	0.4485	1.1732	1.0545	0.0307*
H182	0.6113	1.2527	1.0432	0.0307*

H183	0.6244	1.0955	1.0543	0.0307*	
H1011	0.3901	0.3375	0.8936	0.0210*	
H1021	0.5458	0.3044	0.8401	0.0227*	
H1031	0.2864	0.1925	0.8403	0.0216*	
H1041	0.1475	0.4332	0.8071	0.0208*	
H1051	0.1027	0.3204	0.8814	0.0205*	
H1071	−0.0618	0.5159	0.8943	0.0277*	
H1072	−0.1496	0.4265	0.8634	0.0277*	
H1073	−0.0510	0.5631	0.8522	0.0277*	
H1171	0.4106	0.4051	0.9533	0.0248*	
H1161	0.4328	0.5057	1.0127	0.0242*	
H1141	0.6811	0.8373	0.9692	0.0251*	
H1131	0.6631	0.7359	0.9092	0.0262*	
H1181	0.6853	0.7743	1.0403	0.0293*	
H1182	0.4977	0.8308	1.0360	0.0293*	
H1183	0.5272	0.6785	1.0533	0.0293*	
H372	0.7175	0.3410	0.7546	0.0500*	
H1111	0.5558	0.5709	0.8710	0.0500*	
H91	0.3752	0.6304	0.7898	0.0500*	
H101	0.5500	0.9544	0.7953	0.0500*	
H1091	0.3765	0.1308	0.7891	0.0500*	
H111	0.5487	1.0651	0.8696	0.0500*	
H381	0.2908	0.3414	0.7478	0.0500*	
H1101	0.5725	0.4538	0.7976	0.0500*	
H82	0.0225	0.7024	0.7861	0.0500*	0.5000
H373	0.8299	0.3342	0.7840	0.0500*	0.5000
H1082	0.0378	0.2079	0.7898	0.0500*	0.5000
H1081	−0.0768	0.3020	0.8047	0.0500*	0.5000
H81	−0.0855	0.7916	0.8003	0.0500*	0.5000
H382	0.1846	0.3361	0.7149	0.0500*	0.5000
H392	0.9679	0.6394	0.7341	0.0500*	0.5000
H371	0.8159	0.4684	0.7636	0.0500*	0.5000
H391	1.0542	0.6375	0.7630	0.0500*	0.5000
H393	0.9240	0.5342	0.7539	0.0500*	0.5000
H383	0.2028	0.4668	0.7360	0.0500*	0.5000
H394	1.1194	0.5651	0.7443	0.0500*	0.5000

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0161 (7)	0.0187 (7)	0.0158 (7)	0.0007 (6)	0.0006 (6)	−0.0003 (6)
C2	0.0162 (7)	0.0155 (7)	0.0167 (7)	0.0015 (6)	−0.0001 (6)	0.0018 (6)
C3	0.0188 (7)	0.0169 (7)	0.0120 (7)	0.0024 (6)	0.0011 (6)	−0.0013 (6)
C4	0.0156 (7)	0.0155 (7)	0.0141 (7)	0.0003 (6)	−0.0013 (5)	−0.0010 (6)
C5	0.0168 (7)	0.0171 (7)	0.0143 (7)	0.0004 (6)	0.0011 (6)	−0.0011 (6)
O6	0.0150 (5)	0.0167 (5)	0.0193 (6)	0.0007 (4)	−0.0004 (4)	−0.0024 (5)
C7	0.0164 (7)	0.0248 (8)	0.0218 (8)	0.0024 (7)	0.0023 (6)	−0.0025 (7)
O8	0.0175 (6)	0.0207 (6)	0.0214 (6)	−0.0006 (5)	−0.0032 (5)	−0.0028 (5)

O9	0.0240 (6)	0.0199 (5)	0.0142 (5)	0.0055 (5)	0.0000 (5)	−0.0030 (4)
O10	0.0191 (5)	0.0180 (5)	0.0186 (5)	0.0020 (5)	0.0054 (4)	0.0023 (4)
N11	0.0201 (6)	0.0254 (7)	0.0160 (6)	−0.0059 (6)	0.0008 (5)	−0.0015 (6)
C12	0.0163 (7)	0.0165 (7)	0.0163 (7)	0.0023 (6)	−0.0012 (6)	0.0001 (6)
C13	0.0166 (7)	0.0185 (7)	0.0209 (8)	−0.0009 (6)	0.0018 (6)	−0.0005 (6)
C14	0.0168 (7)	0.0197 (7)	0.0231 (8)	−0.0002 (6)	−0.0024 (6)	−0.0032 (6)
C15	0.0186 (7)	0.0197 (7)	0.0176 (7)	0.0042 (6)	−0.0027 (6)	−0.0018 (6)
C16	0.0191 (7)	0.0208 (8)	0.0187 (7)	−0.0003 (7)	0.0020 (6)	0.0003 (6)
C17	0.0152 (7)	0.0212 (8)	0.0207 (7)	−0.0018 (6)	0.0000 (6)	−0.0016 (6)
C18	0.0226 (8)	0.0318 (9)	0.0180 (8)	0.0013 (8)	−0.0021 (6)	−0.0036 (7)
C101	0.0141 (6)	0.0185 (7)	0.0167 (7)	0.0008 (6)	−0.0009 (6)	0.0008 (6)
C102	0.0174 (7)	0.0159 (7)	0.0172 (7)	0.0021 (6)	0.0010 (6)	0.0017 (6)
C103	0.0185 (7)	0.0153 (7)	0.0158 (7)	0.0027 (6)	0.0018 (6)	−0.0001 (6)
C104	0.0157 (7)	0.0163 (7)	0.0153 (7)	0.0006 (6)	−0.0005 (6)	−0.0005 (6)
C105	0.0158 (7)	0.0176 (7)	0.0157 (7)	−0.0008 (6)	0.0009 (6)	0.0010 (6)
O106	0.0136 (5)	0.0170 (5)	0.0192 (6)	0.0016 (4)	−0.0002 (4)	−0.0014 (5)
C107	0.0162 (7)	0.0247 (8)	0.0219 (8)	0.0029 (7)	0.0010 (6)	−0.0009 (7)
O108	0.0178 (6)	0.0214 (5)	0.0228 (6)	−0.0006 (5)	−0.0032 (5)	−0.0016 (5)
O109	0.0278 (6)	0.0196 (5)	0.0156 (5)	0.0066 (5)	0.0008 (5)	−0.0033 (4)
O110	0.0191 (5)	0.0177 (5)	0.0210 (5)	0.0021 (5)	0.0062 (4)	0.0039 (5)
N111	0.0159 (6)	0.0223 (7)	0.0191 (7)	−0.0018 (5)	0.0001 (5)	0.0007 (5)
C112	0.0113 (6)	0.0194 (7)	0.0210 (7)	0.0020 (6)	−0.0022 (6)	0.0002 (6)
C117	0.0158 (7)	0.0192 (7)	0.0227 (8)	−0.0002 (6)	−0.0007 (6)	0.0003 (6)
C116	0.0157 (7)	0.0222 (8)	0.0208 (7)	0.0012 (6)	−0.0001 (6)	0.0030 (6)
C115	0.0163 (7)	0.0218 (8)	0.0220 (8)	0.0037 (6)	−0.0029 (6)	−0.0011 (7)
C114	0.0167 (7)	0.0193 (8)	0.0260 (8)	−0.0008 (6)	−0.0034 (7)	0.0010 (7)
C113	0.0176 (7)	0.0224 (8)	0.0226 (8)	−0.0004 (7)	−0.0003 (6)	0.0025 (6)
C118	0.0237 (8)	0.0228 (9)	0.0235 (8)	0.0012 (7)	−0.0018 (7)	−0.0020 (7)
O37	0.0192 (5)	0.0238 (6)	0.0182 (5)	0.0011 (5)	0.0016 (4)	−0.0017 (5)
O38	0.0180 (5)	0.0232 (6)	0.0190 (5)	−0.0005 (5)	0.0011 (4)	0.0016 (5)
O39	0.0232 (6)	0.0203 (6)	0.0198 (6)	−0.0012 (5)	−0.0023 (5)	−0.0002 (4)

Geometric parameters (Å, º)

C1—C2	1.529 (2)	C102—O110	1.4373 (19)
C1—O6	1.4476 (18)	C102—H1021	1.000
C1—N11	1.413 (2)	C103—C104	1.521 (2)
C1—H11	0.979	C103—O109	1.4349 (18)
C2—C3	1.528 (2)	C103—H1031	0.985
C2—O10	1.4295 (19)	C104—C105	1.538 (2)
C2—H21	0.987	C104—O108	1.4303 (19)
C3—C4	1.518 (2)	C104—H1041	0.993
C3—O9	1.4372 (18)	C105—O106	1.4351 (19)
C3—H31	0.996	C105—C107	1.514 (2)
C4—C5	1.533 (2)	C105—H1051	0.991
C4—O8	1.4269 (19)	C107—H1071	0.971
C4—H41	0.989	C107—H1072	0.975
C5—O6	1.4311 (19)	C107—H1073	0.982

C5—C7	1.512 (2)	O108—H1082	1.021
C5—H51	0.998	O108—H1081	0.790
C7—H71	0.975	O109—H1091	0.978
C7—H72	0.997	O110—H1101	0.985
C7—H73	0.980	N111—C112	1.408 (2)
O8—H82	0.955	N111—H1111	0.931
O8—H81	0.770	C112—C117	1.395 (2)
O9—H91	0.970	C112—C113	1.398 (2)
O10—H101	0.927	C117—C116	1.393 (2)
N11—C12	1.401 (2)	C117—H1171	0.996
N11—H111	0.929	C116—C115	1.395 (2)
C12—C13	1.394 (2)	C116—H1161	0.979
C12—C17	1.397 (2)	C115—C114	1.395 (2)
C13—C14	1.392 (2)	C115—C118	1.509 (2)
C13—H131	0.983	C114—C113	1.387 (2)
C14—C15	1.393 (2)	C114—H1141	0.993
C14—H141	0.974	C113—H1131	0.983
C15—C16	1.390 (2)	C118—H1181	0.997
C15—C18	1.507 (2)	C118—H1182	0.981
C16—C17	1.390 (2)	C118—H1183	0.998
C16—H161	0.987	O37—H372	0.933
C17—H171	1.000	O37—H373	0.979
C18—H181	0.987	O37—H371	0.920
C18—H182	0.975	O38—H381	0.932
C18—H183	0.990	O38—H382	0.977
C101—C102	1.535 (2)	O38—H383	0.884
C101—O106	1.4477 (19)	O39—H392	0.806
C101—N111	1.424 (2)	O39—H391	0.891
C101—H1011	0.971	O39—H393	0.807
C102—C103	1.522 (2)	O39—H394	0.954

C2—C1—O6	110.54 (12)	C101—C102—C103	109.14 (13)
C2—C1—N11	110.51 (13)	C101—C102—O110	109.35 (13)
O6—C1—N11	109.40 (13)	C103—C102—O110	111.85 (13)
C2—C1—H11	108.1	C101—C102—H1021	108.3
O6—C1—H11	107.6	C103—C102—H1021	110.2
N11—C1—H11	110.7	O110—C102—H1021	108.0
C1—C2—C3	109.33 (13)	C102—C103—C104	110.81 (13)
C1—C2—O10	109.69 (13)	C102—C103—O109	110.89 (13)
C3—C2—O10	112.30 (12)	C104—C103—O109	109.61 (13)
C1—C2—H21	108.3	C102—C103—H1031	109.0
C3—C2—H21	109.2	C104—C103—H1031	108.1
O10—C2—H21	107.9	O109—C103—H1031	108.4
C2—C3—C4	110.65 (12)	C103—C104—C105	107.62 (12)
C2—C3—O9	110.77 (13)	C103—C104—O108	109.47 (12)
C4—C3—O9	109.89 (12)	C105—C104—O108	109.90 (13)
C2—C3—H31	109.1	C103—C104—H1041	109.0
C4—C3—H31	107.1	C105—C104—H1041	111.2

O9—C3—H31	109.2	O108—C104—H1041	109.6
C3—C4—C5	107.49 (12)	C104—C105—O106	108.67 (12)
C3—C4—O8	109.94 (12)	C104—C105—C107	112.91 (13)
C5—C4—O8	110.20 (13)	O106—C105—C107	107.79 (13)
C3—C4—H41	109.9	C104—C105—H1051	109.8
C5—C4—H41	110.0	O106—C105—H1051	108.6
O8—C4—H41	109.3	C107—C105—H1051	109.0
C4—C5—O6	107.93 (12)	C101—O106—C105	112.69 (12)
C4—C5—C7	114.03 (13)	C105—C107—H1071	109.6
O6—C5—C7	107.52 (12)	C105—C107—H1072	111.4
C4—C5—H51	108.2	H1071—C107—H1072	108.1
O6—C5—H51	110.1	C105—C107—H1073	110.1
C7—C5—H51	109.1	H1071—C107—H1073	108.2
C1—O6—C5	112.16 (12)	H1072—C107—H1073	109.4
C5—C7—H71	109.9	C104—O108—H1082	111.7
C5—C7—H72	111.4	C104—O108—H1081	117.7
H71—C7—H72	107.3	H1082—O108—H1081	100.9
C5—C7—H73	111.2	C103—O109—H1091	107.1
H71—C7—H73	108.7	C102—O110—H1101	110.2
H72—C7—H73	108.3	C101—N111—C112	123.04 (13)
C4—O8—H82	115.4	C101—N111—H1111	112.3
C4—O8—H81	116.7	C112—N111—H1111	111.9
H82—O8—H81	100.3	N111—C112—C117	122.81 (14)
C3—O9—H91	102.2	N111—C112—C113	118.84 (14)
C2—O10—H101	114.7	C117—C112—C113	118.27 (15)
C1—N11—C12	122.72 (13)	C112—C117—C116	120.02 (15)
C1—N11—H111	116.8	C112—C117—H1171	119.9
C12—N11—H111	118.8	C116—C117—H1171	120.1
N11—C12—C13	119.39 (14)	C117—C116—C115	122.10 (15)
N11—C12—C17	121.78 (14)	C117—C116—H1161	118.1
C13—C12—C17	118.80 (14)	C115—C116—H1161	119.8
C12—C13—C14	120.25 (15)	C116—C115—C114	117.25 (15)
C12—C13—H131	120.1	C116—C115—C118	121.96 (15)
C14—C13—H131	119.6	C114—C115—C118	120.79 (15)
C13—C14—C15	121.48 (15)	C115—C114—C113	121.27 (15)
C13—C14—H141	119.2	C115—C114—H1141	118.6
C15—C14—H141	119.4	C113—C114—H1141	120.1
C14—C15—C16	117.58 (15)	C112—C113—C114	121.07 (15)
C14—C15—C18	121.11 (15)	C112—C113—H1131	119.2
C16—C15—C18	121.30 (15)	C114—C113—H1131	119.7
C15—C16—C17	121.81 (15)	C115—C118—H1181	109.2
C15—C16—H161	120.1	C115—C118—H1182	110.3
C17—C16—H161	118.1	H1181—C118—H1182	109.4
C12—C17—C16	119.99 (15)	C115—C118—H1183	106.7
C12—C17—H171	120.6	H1181—C118—H1183	111.1
C16—C17—H171	119.5	H1182—C118—H1183	110.1
C15—C18—H181	112.9	H372—O37—H373	93.3
C15—C18—H182	108.9	H372—O37—H371	108.5

H181—C18—H182	106.8	H373—O37—H371	104.1
C15—C18—H183	112.3	H381—O38—H382	99.6
H181—C18—H183	108.5	H381—O38—H383	108.2
H182—C18—H183	107.2	H382—O38—H383	105.8
C102—C101—O106	109.99 (12)	H392—O39—H391	94.5
C102—C101—N111	109.26 (13)	H392—O39—H393	106.6
O106—C101—N111	110.04 (13)	H391—O39—H393	122.1
C102—C101—H1011	107.7	H392—O39—H394	112.2
O106—C101—H1011	109.4	H391—O39—H394	73.4
N111—C101—H1011	110.4	H393—O39—H394	136.8

Hydrogen-bond geometry (Å, º)

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) $-x+1, y-1/2, -z+3/2$; (ii) $-x+1, y+1/2, -z+3/2$; (iii) $x, y-1, z$; (iv) $x-1, y, z$; (v) $x+1, y, z$; (vi) $-x, y+1/2, -z+3/2$; (vii) $-x, y-1/2, -z+3/2$.