organic compounds

1-(2-Bromo-2-deoxy-β-D-xylofuranosyl)-uracil

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In the title compound, $C_9H_{11}BrN_2O_5$, the ribofuranose ring has a C2-*exo*, C3-*endo* twist configuration and is attached to the uracil unit *via* a β-N$_1$-glycosidic bond. The crystal structure is stabilized by two intermolecular O—H···O interactions and one intermolecular N—H···O interaction.

Related literature

For the synthesis of the title compound and its analogues, see: Shakya *et al.* (2010). For a related structure, see: Suck *et al.* (1972). For the use of the title compound as a pharmaceutical intermediate, see: Haraguchi *et al.* (1993); Kittaka *et al.* (1992); Pozharskii *et al.* (1997); Sairam *et al.* (2003). For the biological activity of nucleoside derivatives, see: Johar *et al.* (2005).
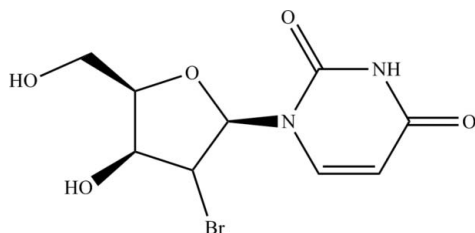
Experimental

Crystal data

$C_9H_{11}BrN_2O_5$
$M_r = 307.11$
Orthorhombic, $P2_12_12_1$
$a = 4.8444$ (3) Å
$b = 12.7237$ (10) Å
$c = 17.4388$ (13) Å

$V = 1074.90$ (13) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 3.84$ mm^{-1}
$T = 296$ K
$0.30 \times 0.20 \times 0.06$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min} = 0.583$, $T_{max} = 0.746$

6683 measured reflections
2091 independent reflections
1956 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.048$
$S = 1.02$
2091 reflections
155 parameters
H-atom parameters constrained

$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}
Absolute structure: Flack (1983), 834 Friedel pairs
Flack parameter: 0.016 (9)

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2B···O4^i	0.82	2.03	2.841 (2)	169
N2—H2C···O3^{ii}	0.86	2.17	2.983 (2)	158
O3—H3B···O5^{iii}	0.82	1.96	2.769 (2)	167

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

Data collection: *SMART* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL*.

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supporting information

1-(2-Bromo-2-deoxy-*β*-D-xylofuranosyl)uracil

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S1. Comment

In the last few decades, there has been dramatic progress in the synthesis of the nucleoside analogues for their biological evaluation of the anticancer activity (Johar *et al.*, 2005; Shakya *et al.*, 2010; Suck *et al.*, 1972). The title compound (I) can be used as important pharmaceutical intermediates (Haraguchi *et al.*, 1993; Kittaka *et al.*, 1992; Pozharskii *et al.*, 1997; Sairam *et al.*, 2003). The synthetic procedure is described below. To know the relative stereochemistry of the anomeric position in the ribofuranose ring, it is necessary to gain the well defined structure of (I) by X-diffraction method. The molecular structure of the title compound is shown in Fig. 1. From the single-crystal structure we observed that the ribofuranose ring has a C2-*exo*, C3-*endo* twist configuration and the anomeric carbons are always *β* configuration in the crystal packing. The crystal structure of (I) is stabilized by two intermolecular O—H···O interactions and one intermolecular N—H···O interaction (Table 1, Fig. 2).

S2. Experimental

All reagents and solvents were used as obtained commercially without further purification. NMR spectra was recorded on Bruker AV 400 MHz NMR spectrometers at ambient temperature. The title compound was prepared according to the reported procedure (Shakya *et al.*, 2010). Detritylation of 1-(3-Bromo-3-deoxy-5-O-trityl-*β*-D-arabinofuranosyl)uracil using 80% aqueous acetic acid (*v*/*v*) at 90 °C for 30 min, then cooled to room temperature, after the solvent were distilled off a white solid of the title compound was obtained in about 70% yield. 1H NMR (400 MHz, DMSO-*d6*): δ 3.65–3.77 (m, 2H, H-5′), 4.26–4.39 (m, 3H, H-2′, H-3′, H-4′), 4.89 (t, *J* = 4.88 Hz, 1H, 5′-OH), 5.64 (dd, *J* = 8.54 and 1.83 Hz, 1H, H-5), 6.04 (d, *J* = 3.05 Hz, 1H, H-1′), 6.09 (d, *J* = 1.83 Hz, 1H, 3′-OH), 7.72 (d, *J* = 7.93 Hz, 1H, H-6), 11.39 (s, 1H, NH). In a sample vial, colorless block-shaped single crystals were grown from DMSO and water (*v*/*v* = 1:1) at room temperature.

S3. Refinement

The N-bound and the C-bound H atoms were positioned geometrically and refined using a riding model: N—H = 0.86 Å and C—H = 0.93–0.98 Å, with $U_{iso}(H) = 1.2U_{iso}(N,C)$; while the O-bound H atoms were placed in idealized positions and constrained to ride on their parent atoms: O—H = 0.82 Å, with $U_{iso}(H) = 1.5$ times $U_{iso}(O)$.
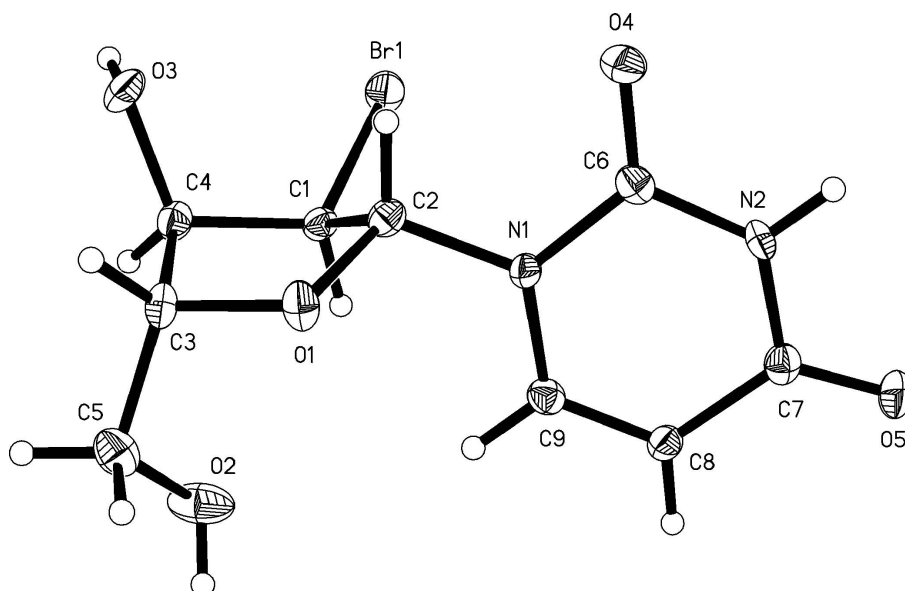
Figure 1

The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.
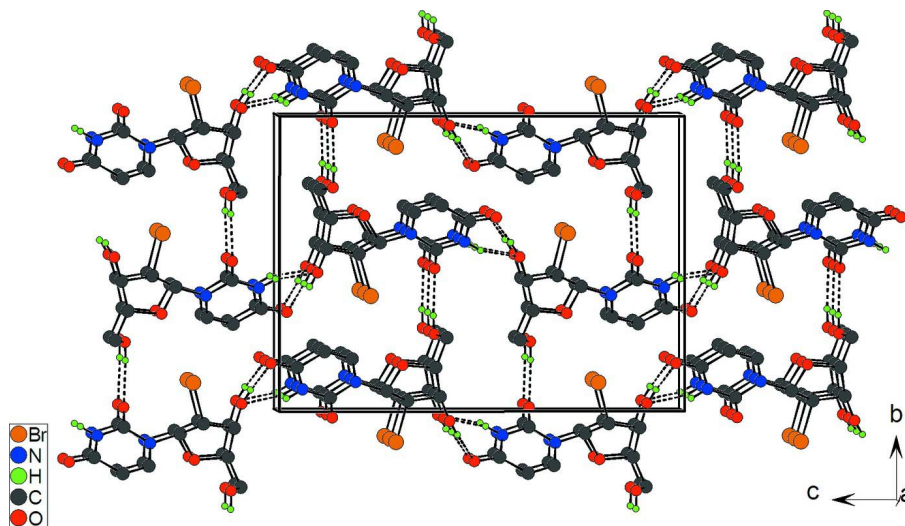
Figure 2

The three-dimensional structure of the title compound formed by intermolecular hydrogen bonds viewed down the *a* axis. The intermolecular hydrogen bonds are shown as dashed lines.

1-(2-Bromo-2-deoxy-*β*-D-xylofuranosyl)uracil

Crystal data

$C_9H_{11}BrN_2O_5$	$c = 17.4388 (13)$ Å
$M_r = 307.11$	$V = 1074.90 (13)$ Å^3
Orthorhombic, $P2_12_12_1$	$Z = 4$
Hall symbol: P 2ac 2ab	$F(000) = 616$
$a = 4.8444 (3)$ Å	$D_x = 1.898$ Mg m^{-3}
$b = 12.7237 (10)$ Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3827 reflections
$\theta = 2.3–26.6°$
$\mu = 3.84$ mm^{-1}

$T = 296$ K
Block, colourless
$0.30 \times 0.20 \times 0.06$ mm

Data collection

Bruker SMART CCD area-detector
   diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan
   (*SADABS*; Bruker, 2008)
$T_{min} = 0.583$, $T_{max} = 0.746$

6683 measured reflections
2091 independent reflections
1956 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 26.0°$, $\theta_{min} = 2.0°$
$h = -5 \rightarrow 5$
$k = -12 \rightarrow 15$
$l = -17 \rightarrow 21$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.048$
$S = 1.02$
2091 reflections
155 parameters
0 restraints
Primary atom site location: structure-invariant
   direct methods
Secondary atom site location: difference Fourier
   map

Hydrogen site location: inferred from
   neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0196P)^2]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}
Absolute structure: Flack (1983), 834 Friedel
   pairs
Absolute structure parameter: 0.016 (9)

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.27277 (5)	−0.100786 (17)	0.715735 (13)	0.03335 (9)
N1	0.5109 (4)	0.10657 (15)	0.81851 (10)	0.0218 (4)
N2	0.4796 (4)	0.08084 (15)	0.94956 (10)	0.0263 (5)
H2C	0.5395	0.0505	0.9904	0.032*
C1	0.3861 (5)	0.04049 (18)	0.68858 (12)	0.0225 (5)
H1A	0.2276	0.0878	0.6937	0.027*
C2	0.6127 (5)	0.07596 (18)	0.74317 (13)	0.0234 (5)
H2A	0.7521	0.0206	0.7484	0.028*
C3	0.6883 (5)	0.15620 (18)	0.62383 (11)	0.0262 (5)
H3A	0.8688	0.1469	0.5994	0.031*
C4	0.5166 (5)	0.0564 (2)	0.61047 (12)	0.0258 (6)

H4A	0.3762	0.0675	0.5708	0.031*
C5	0.5620 (5)	0.2564 (2)	0.59440 (14)	0.0354 (6)
H5A	0.6704	0.3160	0.6115	0.042*
H5B	0.5616	0.2560	0.5388	0.042*
C6	0.6060 (5)	0.05312 (19)	0.88240 (13)	0.0241 (5)
C7	0.2656 (5)	0.15228 (17)	0.95953 (11)	0.0257 (5)
C8	0.1829 (5)	0.20597 (17)	0.89049 (12)	0.0244 (5)
H8A	0.0460	0.2571	0.8921	0.029*
C9	0.3045 (5)	0.18165 (17)	0.82441 (12)	0.0243 (5)
H9A	0.2486	0.2166	0.7802	0.029*
O1	0.7292 (4)	0.16509 (12)	0.70608 (7)	0.0290 (4)
O2	0.2882 (4)	0.26569 (14)	0.62192 (11)	0.0494 (5)
H2B	0.2448	0.3279	0.6236	0.074*
O3	0.7002 (4)	−0.02551 (13)	0.58996 (8)	0.0339 (4)
H3B	0.6137	−0.0730	0.5692	0.051*
O4	0.7873 (4)	−0.01293 (12)	0.88008 (8)	0.0332 (4)
O5	0.1654 (4)	0.16566 (13)	1.02337 (8)	0.0351 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.03955 (14)	0.02863 (14)	0.03187 (14)	−0.00614 (13)	0.00305 (12)	−0.00212 (10)
N1	0.0252 (9)	0.0242 (11)	0.0162 (9)	0.0052 (10)	−0.0018 (8)	−0.0013 (9)
N2	0.0350 (11)	0.0281 (12)	0.0157 (10)	0.0027 (10)	−0.0039 (9)	0.0051 (9)
C1	0.0248 (12)	0.0197 (12)	0.0229 (12)	0.0001 (10)	0.0001 (9)	−0.0030 (10)
C2	0.0210 (11)	0.0240 (13)	0.0252 (12)	−0.0011 (10)	0.0022 (10)	−0.0032 (10)
C3	0.0255 (13)	0.0352 (14)	0.0178 (11)	−0.0011 (12)	0.0034 (10)	−0.0009 (10)
C4	0.0246 (12)	0.0309 (14)	0.0218 (12)	0.0025 (12)	−0.0003 (10)	−0.0023 (11)
C5	0.0363 (15)	0.0342 (15)	0.0357 (15)	−0.0072 (13)	−0.0011 (12)	0.0064 (13)
C6	0.0268 (13)	0.0207 (13)	0.0247 (13)	−0.0053 (12)	−0.0044 (10)	0.0017 (11)
C7	0.0277 (13)	0.0260 (12)	0.0235 (11)	−0.0059 (12)	−0.0005 (12)	−0.0015 (9)
C8	0.0265 (13)	0.0241 (12)	0.0225 (12)	0.0026 (11)	−0.0018 (10)	−0.0030 (10)
C9	0.0251 (13)	0.0232 (12)	0.0245 (12)	−0.0002 (11)	−0.0046 (10)	0.0008 (10)
O1	0.0332 (9)	0.0331 (9)	0.0208 (7)	−0.0096 (9)	0.0003 (9)	0.0002 (6)
O2	0.0309 (11)	0.0294 (9)	0.0879 (14)	−0.0012 (10)	0.0003 (11)	0.0049 (9)
O3	0.0382 (10)	0.0327 (9)	0.0309 (9)	0.0040 (9)	0.0079 (8)	−0.0120 (7)
O4	0.0367 (10)	0.0306 (9)	0.0323 (9)	0.0106 (10)	−0.0057 (9)	0.0008 (7)
O5	0.0433 (11)	0.0416 (11)	0.0203 (8)	0.0005 (9)	0.0073 (8)	0.0001 (8)

Geometric parameters (Å, º)

Br1—C1	1.938 (2)	C3—H3A	0.9800
N1—C6	1.384 (3)	C4—O3	1.416 (3)
N1—C9	1.387 (3)	C4—H4A	0.9800
N1—C2	1.456 (3)	C5—O2	1.416 (3)
N2—C6	1.368 (3)	C5—H5A	0.9700
N2—C7	1.390 (3)	C5—H5B	0.9700
N2—H2C	0.8600	C6—O4	1.216 (3)

C1—C4	1.515 (3)	C7—O5	1.226 (2)
C1—C2	1.522 (3)	C7—C8	1.441 (3)
C1—H1A	0.9800	C8—C9	1.331 (3)
C2—O1	1.422 (3)	C8—H8A	0.9300
C2—H2A	0.9800	C9—H9A	0.9300
C3—O1	1.452 (2)	O2—H2B	0.8200
C3—C5	1.504 (4)	O3—H3B	0.8200
C3—C4	1.536 (3)		
C6—N1—C9	121.24 (18)	C1—C4—C3	101.55 (17)
C6—N1—C2	118.83 (18)	O3—C4—H4A	111.3
C9—N1—C2	119.68 (17)	C1—C4—H4A	111.3
C6—N2—C7	127.57 (18)	C3—C4—H4A	111.3
C6—N2—H2C	116.2	O2—C5—C3	109.7 (2)
C7—N2—H2C	116.2	O2—C5—H5A	109.7
C4—C1—C2	102.81 (19)	C3—C5—H5A	109.7
C4—C1—Br1	117.50 (16)	O2—C5—H5B	109.7
C2—C1—Br1	109.06 (15)	C3—C5—H5B	109.7
C4—C1—H1A	109.0	H5A—C5—H5B	108.2
C2—C1—H1A	109.0	O4—C6—N2	122.0 (2)
Br1—C1—H1A	109.0	O4—C6—N1	123.6 (2)
O1—C2—N1	109.36 (18)	N2—C6—N1	114.4 (2)
O1—C2—C1	103.78 (18)	O5—C7—N2	119.96 (19)
N1—C2—C1	113.54 (18)	O5—C7—C8	125.7 (2)
O1—C2—H2A	110.0	N2—C7—C8	114.38 (18)
N1—C2—H2A	110.0	C9—C8—C7	119.4 (2)
C1—C2—H2A	110.0	C9—C8—H8A	120.3
O1—C3—C5	109.06 (19)	C7—C8—H8A	120.3
O1—C3—C4	106.75 (17)	C8—C9—N1	122.9 (2)
C5—C3—C4	115.4 (2)	C8—C9—H9A	118.5
O1—C3—H3A	108.5	N1—C9—H9A	118.5
C5—C3—H3A	108.5	C2—O1—C3	109.45 (16)
C4—C3—H3A	108.5	C5—O2—H2B	109.5
O3—C4—C1	112.99 (19)	C4—O3—H3B	109.5
O3—C4—C3	107.85 (18)		

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
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