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1,6-Anhydro-2-iodo-2-deoxy-*β*-D-glucopyranose (Iodolevoglucosan)

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.004 Å
R factor = 0.020
wR factor = 0.049
Data-to-parameter ratio = 18.2

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

The molecular structure of the title compound, $C_6H_9IO_4$, is similar to that of 1,6-anhydro-*β*-D-glucopyranose. The crystal packing shows strong intermolecular O—H···O and C—H···I hydrogen bonds.

Comment

1,6-Anhydro sugars have been shown to be convenient starting materials for the synthesis of carbon-branched deoxysugars (Cerny, 1994; Hanessian, 1983; Witczak, 1994; Witczak & Li, 1995). They are easily transformed into 1,6:2,3- or 1,6:3,4-anhydropyranoses ('Cerny-epoxides'; Cerny, 1994), which show a rigid cyclic framework, suitable for stereo- and regioselective *trans*-diaxial opening by several nucleophiles such as Grignard reagents. In our synthesis of C-2 branched sugars, we prepared 1,6-anhydro-2-iodo-2-desoxy-*β*-D-glucopyranose (Iodolevoglucosan), (I), from commercially available D-glucal.

(I)
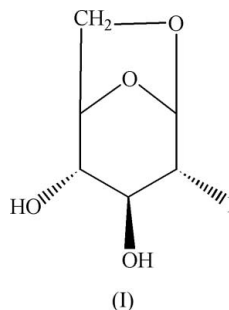
The molecular structure of (I) is similar to that of 1,6-anhydro-*β*-D-glucopyranose (Park *et al.*, 1971) with one OH group substituted by iodine, so the hydroxyl groups together with the iodine ligand are all in axial positions. The C1—I1 bond length is 2.157 (3) Å; other geometric parameters of non-H atoms are not significantly different from those of the glucopyranose and thus need no further discussion. The crystal packing shows a three-dimensional network, with a complex hydrogen-bonding pattern consisting of intermolecular O—H···O and C—H···I interactions (Fig. 2 and Table 2).

Experimental

D-Glucal (12,5 g, 0.086 mol) was mixed with powdered dried molecular sieves (4 Å, 36 g) and bis(tributyltin) oxide (34.9 ml, 0.069 mol, 0.8 equivalents) in refluxing acetonitrile for 5 h. After cooling to 273 K, iodine (33.8 g, 3 equivalents) was added in portions and the mixture was stirred for an additional 3 h at room temperature. Work-up was carried out by filtration and evaporation of the volatile
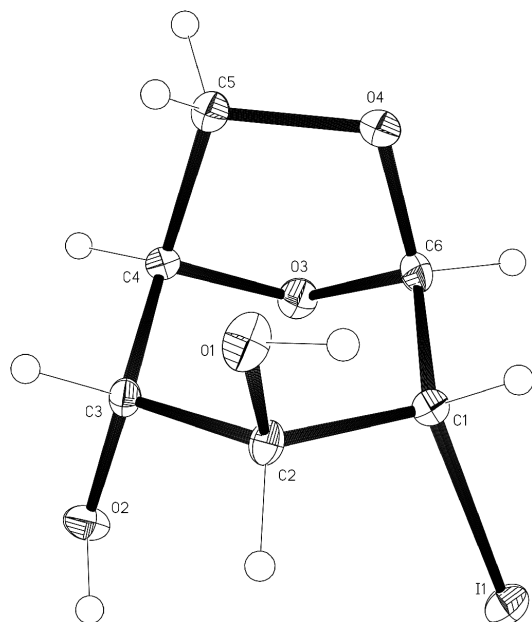
NMR (125 MHz, MeOD): δ 27.1 (d, C-2), 65.6 (t, C-6), 72.5 (d, C-4), 75.1 (d, C-3), 76.5 (d, C-5), 103.7 (d, C-1). MS (EI, 70 eV): m/z (%) 272 (5) $[M^+]$, 253 (10), 182 (22), 169 (100), 127 (10), 99 (28), 89 (70), 57 (70), 43 (39).

Crystal data

$C_6H_9IO_4$	Mo $K\alpha$ radiation
$M_r = 272.03$	Cell parameters from 4124
Orthorhombic, $P2_12_12_1$	reflections
$a = 6.0641$ (5) Å	$\theta = 2.6$–$28.2°$
$b = 10.6966$ (9) Å	$\mu = 4.17$ mm^{-1}
$c = 11.7335$ (10) Å	$T = 120$ (2) K
$V = 761.10$ (11) Å^3	Block, colourless
$Z = 4$	$0.22 \times 0.20 \times 0.15$ mm
$D_x = 2.374$ Mg m^{-3}	

Data collection

Bruker SMART CCD area-detector diffractometer	1852 independent reflections
φ and ω scans	1793 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)	$R_{int} = 0.027$
$T_{min} = 0.428$, $T_{max} = 0.533$	$\theta_{max} = 28.1°$
7086 measured reflections	$h = -7 \rightarrow 8$
	$k = -13 \rightarrow 14$
	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0289P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.020$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$wR(F^2) = 0.050$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.04$	$\Delta\rho_{max} = 0.81$ e Å^{-3}
1852 reflections	$\Delta\rho_{min} = -0.36$ e Å^{-3}
102 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	754 Friedel pairs
	Flack parameter = 0.02 (3)

Table 1
Selected geometric parameters (Å, °).

I1—C1	2.157 (3)	O4—C5	1.447 (3)
O1—C2	1.428 (3)	C1—C6	1.526 (4)
O2—C3	1.426 (3)	C1—C2	1.534 (4)
O3—C6	1.413 (4)	C2—C3	1.529 (4)
O3—C4	1.455 (3)	C3—C4	1.514 (4)
O4—C6	1.418 (3)	C4—C5	1.524 (4)
C6—C1—I1	108.10 (19)	C2—C1—I1	111.61 (19)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1···O2^i	0.84	1.98	2.805 (3)	169
O2—H2···O3^{ii}	0.84	2.09	2.891 (3)	160
C3—H3A···I1^{iii}	1.00	3.26	3.885 (3)	122
C4—H4A···I1^{iv}	1.00	3.28	4.004 (3)	131
C5—H5A···I1^{iv}	0.99	3.17	3.968 (3)	139
C6—H6A···I1^{v}	1.00	3.21	3.961 (3)	133

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

H atoms were refined at calculated positions (O—H = 0.84 Å and C—H = 0.99–1.00 Å) and refined as riding on their parent C or O atoms, with isotropic displacement parameters $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(O)$. All hydroxyl O—H bonds were allowed to rotate but not to tip.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve

Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.
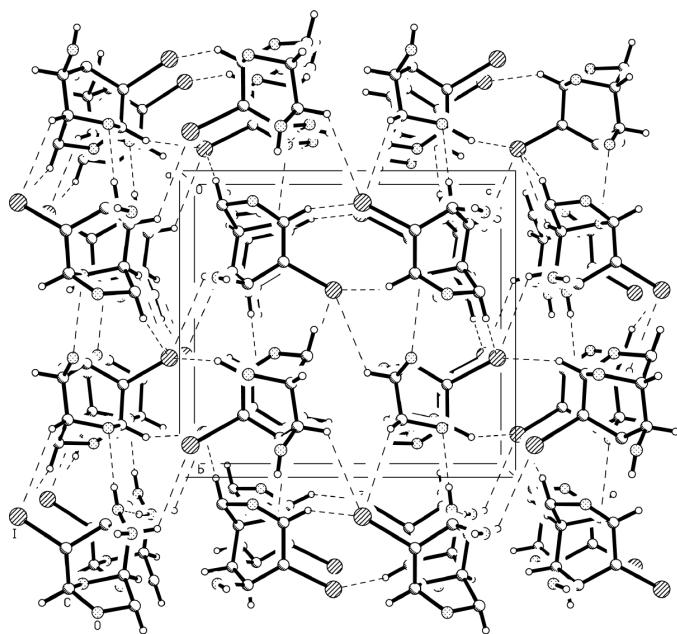

Figure 2
The crystal packing in (I), viewed along [100], with the hydrogen-bonding pattern indicated by dashed lines.

compounds under vacuum. The residue was then treated with aqueous sodium thiosulfate (150 ml) and stirred vigorously. Extraction of the mixture with hexane followed by EtOAc led (after concentration of the EtOAc phase) to a crude product which was filtered over a batch of silica gel and crystallized from methanol to obtain colourless crystals [15.8 g, 0.058 mol, 68%; m.p. = 374 K, literature 374–376 K; $[\alpha]_D = +10.1°$ ($c = 0.92$, MeOH), literature $+10°$ ($c = 1.0$, MeOH)]. ^1H NMR (500 MHz, MeOD): δ 3.64 (s, 1H, 4H), 3.68 (dd, $J_{6a,6b} = 7.3$ Hz, $J_{6a,5} = 5.8$ Hz, 1H, 6a-H,), 3.91 (m, 1H, 2H), 4.14 (m, 1H, 3H), 4.19 (dd, $J_{6a,6b} = 7.3$ Hz, $J_{6b,5} = 1.2$ Hz, 1H, 6b-H), 4.54 (dd, $J_{5,6b} = 1.2$ Hz, $J_{5,6a} = 5.8$ Hz,1H, 5H), 5.69 (s, 1H, 1H). ^{13}C

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structure: *SHELXTL* (Bruker, 2002); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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