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Per(3-deoxy)-α-cyclomannin: an *n*-butanol hexahydrate inclusion complex

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Key indicators

Single-crystal X-ray study
T = 211 K
Mean σ(C–C) = 0.005 Å
H-atom completeness 88%
Disorder in solvent or counterion
R factor = 0.039
wR factor = 0.076
Data-to-parameter ratio = 8.3

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

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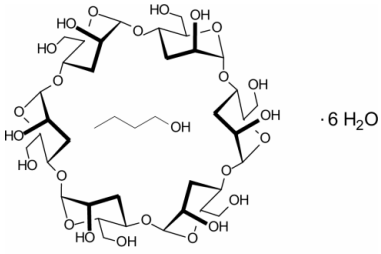
The host molecule in the title compound, cyclohexakis-[(1→4)-3-deoxy-α-D-*arabino*-hexopyranosyl] *n*-butanol hexahydrate, $C_{36}H_{60}O_{24}\cdot C_4H_{10}O\cdot 6H_2O$, has a cavity similar in diameter but smaller in torus height than that of α-cyclodextrin, due to the axial C-2-hydroxyl groups pointing away from the ring plane. The molecules have approximate C_6 symmetry and pack into stacks with channels occupied by disordered *n*-butanol molecules. Water of srystallization fills the space between the stacks. The structure was determined at 211 K.

Comment

Cyclodextrins are of commercial and theoretical interest because of their ability to host hydrophobic organic molecules in their cavities (Szejtli, 1998). Cyclic oligosaccharides derived from sugars other than glucose should have cavities differing in size and hydrophobicity from those of the cyclodextrins and thus in their host specificities. Several new cyclo-oligosaccharides have been sythesized and characterized (Fujita *et al.*, 1995; Nogami *et al.*, 1997; Gattuso *et al.*, 1998; Immel *et al.*, 2000), yet none of these has exhibited, until now, any inclusion complexation behaviour.



(I)

With the per(3-deoxy)-α-cyclomannin-*n*-butanol hexahydrate inclusion complex, (I), we describe the first inclusion compound of a non-glucose cyclooligosaccharide. Similar to α-cyclomannin (Lichtenthaler & Immel, 1994), the per(3-deoxy)-α-cyclomannin molecule has a cavity with an average diameter of 4.50 Å and a height of 7.4 Å, based on the solvent-accessible surface calculated by *MolArch+* (Immel, 2002). The diameter of the cavity is about the same as in α-cyclodextrin; its torus height, however, is significantly smaller than that for α-cyclodextrin (7.9 Å; Saenger *et al.*, 1998), due to the fact that the only secondary hydroxyl group per unit at the wider opening of the torus is axially oriented, and, hence, points diametrically away from the plane of the macrocyclic ring. In the crystal structure, the hexasaccharide units are stacked

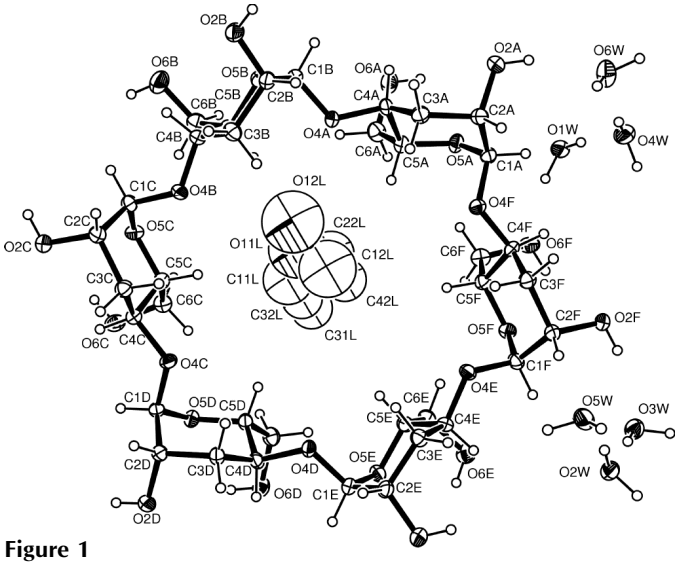


Figure 1
A view of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

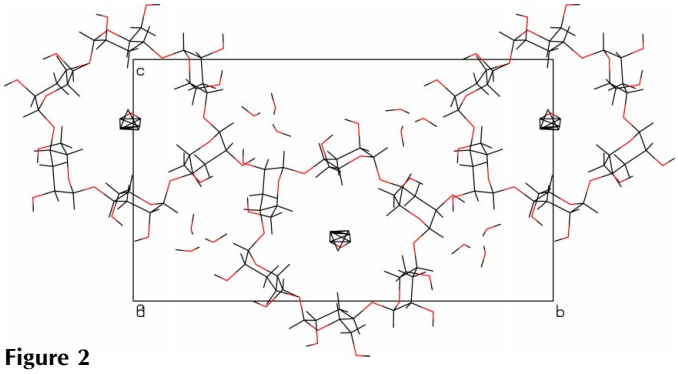


Figure 2
A packing diagram of (I), viewed along the *a* axis. H atoms have been omitted.

along the *a* axis, on top of each other, with the cavities forming channels filled with disordered *n*-butanol molecules. The stacks are connected by hydrogen bonds and water molecules of crystallization fill the space in between.

Experimental

The title compound was synthesized by hydride opening of the epoxide rings in 2,3-anhydro-α-cyclomannin, as described elsewhere (Fujita *et al.*, 1995; Yang *et al.*, 2003). Colourless crystals were obtained by adding a small amount of *n*-butanol to an aqueous solution of per(3-deoxy)-α-cyclomannin, which resulted in a precipitate that redissolved upon addition of ethanol, from which crystals of (I) gradually appeared.

Crystal data

$C_{36}H_{60}O_{24}\cdot C_4H_{10}O\cdot 6H_2O$
M_r = 1059.06
Monoclinic, $P2_1$
a = 7.3995 (5) Å
b = 24.4481 (18) Å
c = 14.2649 (8) Å
β = 99.116 (5)°
V = 2548.0 (3) Å^3
Z = 2
D_x = 1.380 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 36831 reflections
θ = 1.5–27.1°
μ = 0.12 mm^{-1}
T = 211 (2) K
Plate, colourless
0.28 × 0.28 × 0.12 mm

Data collection

Stoe IPDS-II diffractometer
φ scans
36831 measured reflections
5703 independent reflections
3750 reflections with $I > 2\sigma(I)$
R_{int} = 0.077
θ_{max} = 27.1°
$h = -9 \rightarrow 9$
$k = -31 \rightarrow 31$
$l = -17 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.076
S = 0.99
5703 reflections
684 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0181 (8)

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

D—H···A	D—H	H···A	D···A	D—H···A
O2*A*—H2O1···O6*W*	0.83	2.05	2.850 (4)	160
O6*A*—H6O1···O2*C*^{i}	0.83	1.90	2.710 (4)	164
O2*B*—H2O2···O2*W*^{ii}	0.83	1.95	2.753 (4)	162
O6*B*—H6O2···O4*W*^{iii}	0.83	2.09	2.796 (4)	143
O2*C*—H2O3···O1*W*^{iii}	0.83	2.05	2.861 (4)	166
O6*C*—H6O3···O2*A*^{iii}	0.83	1.87	2.696 (4)	174
O2*D*—H2O4···O5*W*^{iv}	0.83	2.07	2.864 (4)	161
O6*D*—H6O4···O2*F*^{v}	0.83	1.96	2.791 (4)	178
O2*E*—H2O5···O2*B*^{vi}	0.83	1.94	2.705 (4)	152
O6*E*—H6O5···O6*B*^{vi}	0.83	1.88	2.682 (4)	162
O2*F*—H2O6···O3*W*	0.83	2.06	2.864 (4)	163
O6*F*—H6O6···O2*D*^{vii}	0.83	1.94	2.770 (3)	174
O1*W*—H11*W*···O4*W*	0.91 (2)	1.93 (2)	2.833 (4)	174 (3)
O1*W*—H12*W*···O6*F*	0.90 (2)	1.82 (2)	2.698 (4)	165 (4)
O2*W*—H21*W*···O6*A*^{viii}	0.91 (2)	1.79 (2)	2.696 (4)	173 (4)
O2*W*—H22*W*···O5*W*	0.89 (2)	1.89 (2)	2.769 (4)	168 (4)
O3*W*—H31*W*···O2*W*	0.91 (2)	1.93 (2)	2.835 (4)	177 (4)
O3*W*—H32*W*···O6*C*^{vii}	0.91 (2)	1.88 (2)	2.762 (4)	165 (4)
O4*W*—H41*W*···O6*W*	0.91 (2)	1.98 (2)	2.862 (5)	164 (4)
O4*W*—H42*W*···O6*D*^{vii}	0.90 (2)	1.90 (2)	2.784 (4)	178 (4)
O5*W*—H51*W*···O6*E*^{ix}	0.88 (2)	1.87 (2)	2.732 (4)	168 (4)
O5*W*—H52*W*···O3*W*^{ix}	0.90 (2)	2.13 (2)	2.976 (4)	157 (4)
O6*W*—H61*W*···O1*W*^{ix}	0.92 (2)	1.90 (2)	2.821 (4)	172 (4)
O6*W*—H62*W*···O2*E*^{x}	0.89 (2)	1.88 (2)	2.741 (4)	163 (4)

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

The refinement was carried out with merged Friedel pairs, as no determination of the absolute configuration is possible in the absence of significant anomalous scattering. The H atoms of per(3-deoxy)-α-cyclomannin were treated as riding atoms. The positions of the water H atoms were found in a difference Fourier map and refined with restrained O—H distances. The butanol molecule in the cavity is completely disordered. Its position is approximated by two sets of five C/O atoms, which were refined isotropically with distance and angle restraints. No H atoms were included; disordered H atoms did not improve the refinement.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

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