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Structure of β-D-Allose, $C_6H_{12}O_6$

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Abstract. $M_r = 180.09$, orthorhombic, $P2_12_12_1$, $a = 4.918$ (1), $b = 11.925$ (2), $c = 12.805$ (2) Å, $V = 751.0$ (2) Å^3, $Z = 4$, $D_x = 1.593$ (1) g cm^{-3}, λ(Mo $K\alpha$) $= 0.71069$ Å, $\mu = 0.96$ cm^{-1}, $F(000) = 384$, $T = 294$ K. Final $R = 0.029$ for 662 unique observed reflexions. The molecule has the $^4C_1$ pyranose chair conformation. The hydroxymethyl group has the *gauche–gauche* conformation. Each β-D-allose molecule is surrounded by eight symmetry-related molecules through hydrogen bonding. All five hydroxyl groups serve as proton donors. Four of the hydroxyl groups and the ring oxygen act as proton acceptors. The anomeric O atom is twice an acceptor which is a very unusual observation.

Introduction. β-D-Allose is a member of the class of common D-aldohexoses of which, presumably owing to its poor crystallization habit, no crystallographic structural data are available. Up to now only derivatives of D-allose, 1,6-anhydro-β-D-allose (Norrestam, Bock & Pedersen, 1981) and 2,6-dideoxy-β-D-allose (Kanters, Batenburg, Gaykema & Roelofsen, 1978) have been studied. According to the literature (Ferrier, 1983) D-allose occurs in the leaves of plants as substituted aryl glycosides. We have undertaken the structure determination as part of our research project on the conformation of saccharides.

Experimental. Crystals grown from a sample obtained from the Bio-Organic Chemistry Group of the Rijksuniversiteit Utrecht. As conventional crystallization techniques failed, a newly developed procedure based on a method described by McPherson (1976) was applied. 25 µl of a solution containing 250 mg D-allose per ml water–ethanol (50:50) was equilibrated against water–ethanol (10:90) using the sitting-drop vapour-phase diffusion method. After four weeks small needle-shaped crystals ($\varnothing < 0.01$ mm) appeared, which were used as seeds in the next step. First 50 µl of a solution containing 250 mg D-allose per ml water–ethanol (50:50) was equilibrated against water–ethanol (25:75). After two weeks no crystals could be observed and the seeds were added. Successive equilibration against water–ethanol (20:80) and water–ethanol (15:85), for two weeks each, yielded crystals of sufficient size.

Crystal dimensions $0.24 \times 0.62 \times 0.07$ mm. Enraf–Nonius CAD-4 automatic diffractometer. Lattice dimensions determined by least squares on 14 reflexions. Systematic absences, $h00$ with $h = 2n+1$, $0k0$ with $k = 2n+1$ and $00l$ with $l = 2n+1$, indicating $P2_12_12_1$. Reflexions measured up to $\theta = 25°$, Mo $K\alpha$ radiation, ω–2θ scan mode, $\Delta\omega = (1.0 + 0.35 \tan\theta)°$, in one half of the reflexion sphere, $h \pm k \pm l$ (max. 5, 14, 15), 2983 reflexions, 803 unique reflexions, $R_{int} = 0.052$, 662 with $I \geq 2.5\sigma(I)$ used for structure determination, four standard reflexions: mean deviations less than 1%, Lp correction applied, no correction for absorption. Structure solved by direct methods with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Final structure obtained by minimizing $\sum w(\Delta F)^2$ with *SHELX*76 (Sheldrick, 1976). Scattering factors for C and O from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). All H atoms located by difference Fourier synthesis. C- and O-atom positions refined using anisotropic thermal parameters. Full-matrix least-squares refinement gave final $R = 0.029$, $R_w = 0.033$ with $w = 1/[\sigma^2(F_o) + 0.002335\,F_o^2]$, $S = 0.69$. Final difference Fourier map showed no peaks above the level ± 0.21 e Å^{-3}. Max. Δ/σ for C and O parameters 0.007, for H 0.022.

Discussion. The final atomic positions and isotropic thermal parameters are given in Table 1.* The conformation of β-D-allose and the atomic numbering are shown in Fig. 1. Bond distances and angles involving C and O atoms and torsion angles are listed in Table 2.

Geometrical features of bond distances and angles are similar to those of other saccharides (Arnott & Scott, 1972). The geometries involving atoms of the hemiacetal sequence C(5)—O(5)—C(1)—O(1) are in keeping with the anomeric effect (Eliel, Allinger, Angyal & Morrison, 1965; Jeffrey, 1979). Particularly, the short anomeric C(1)—O(1) distance [1·386 (4) Å] and the small angle O(5)—C(1)—O(1) [107·0 (3)°] are

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39508 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and isotropic thermal parameters* ($Å^2$) *with e.s.d.'s in parentheses for β-D-allose*

	x	y	z	$U_{eq}\dagger/U$
O(1)	0·5217 (5)	0·4413 (2)	0·3020 (2)	0·0339 (7)
O(2)	0·5132 (6)	0·6757 (2)	0·3683 (2)	0·0341 (7)
O(3)	0·7889 (4)	0·6233 (2)	0·5561 (2)	0·0313 (7)
O(4)	0·4680 (5)	0·5361 (2)	0·7212 (2)	0·0357 (7)
O(5)	0·4638 (5)	0·3887 (2)	0·4705 (1)	0·0285 (6)
O(6)	0·1553 (5)	0·3066 (2)	0·6570 (2)	0·0371 (7)
C(1)	0·5680 (6)	0·4751 (3)	0·4040 (2)	0·0261 (8)
C(2)	0·4296 (6)	0·5854 (2)	0·4333 (2)	0·0251 (8)
C(3)	0·5009 (6)	0·6123 (2)	0·5462 (2)	0·0255 (8)
C(4)	0·4083 (6)	0·5161 (3)	0·6139 (2)	0·0261 (9)
C(5)	0·5357 (7)	0·4061 (3)	0·5789 (2)	0·0268 (9)
C(6)	0·4418 (8)	0·3063 (3)	0·6409 (3)	0·036 (1)
H(C1)	0·775 (6)	0·480 (2)	0·409 (2)	0·013 (7)
H(C2)	0·235 (8)	0·575 (3)	0·429 (3)	0·032 (8)
H(C3)	0·411 (6)	0·678 (3)	0·571 (2)	0·021 (8)
H(C4)	0·220 (7)	0·511 (2)	0·610 (2)	0·014 (7)
H(C5)	0·741 (8)	0·406 (3)	0·587 (2)	0·030 (9)
H(C6)	0·543 (8)	0·307 (3)	0·709 (3)	0·038 (9)
H'(C6)	0·491 (8)	0·238 (3)	0·599 (3)	0·04 (1)
H(O1)	0·33 (1)	0·451 (6)	0·284 (5)	0·12 (2)
H(O2)	0·45 (1)	0·667 (4)	0·305 (4)	0·07 (1)
H(O3)	0·827 (8)	0·691 (3)	0·578 (3)	0·035 (9)
H(O4)	0·64 (1)	0·556 (4)	0·725 (4)	0·06 (1)
H(O6)	0·10 (1)	0·247 (5)	0·627 (4)	0·07 (2)

$\dagger\ U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j.$
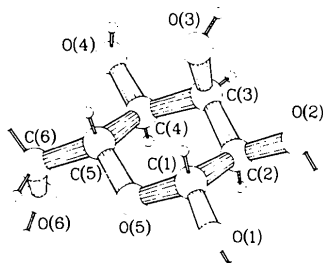

Fig. 1. Molecular conformation and atomic numbering of β-D-allose.

Table 2. *Bond distances* (Å), *bond angles* (°) *and torsion angles* (°) *for β-D-allose*

O(1)—C(1)	1·386 (4)	O(6)—C(6)	1·424 (5)
O(2)—C(2)	1·422 (4)	C(1)—C(2)	1·528 (4)
O(3)—C(3)	1·428 (4)	C(2)—C(3)	1·522 (4)
O(4)—C(4)	1·425 (4)	C(3)—C(4)	1·508 (4)
O(5)—C(1)	1·432 (4)	C(4)—C(5)	1·521 (5)
O(5)—C(5)	1·447 (3)	C(5)—C(6)	1·503 (5)

C(1)—O(5)—C(5)	112·3 (2)	C(2)—C(3)—C(4)	108·4 (2)
O(1)—C(1)—O(5)	107·0 (3)	O(4)—C(4)—C(3)	111·4 (3)
O(1)—C(1)—C(2)	114·1 (2)	O(4)—C(4)—C(5)	110·1 (2)
O(5)—C(1)—C(2)	108·3 (2)	C(3)—C(4)—C(5)	111·2 (2)
O(2)—C(2)—C(1)	112·3 (2)	O(5)—C(5)—C(4)	107·8 (3)
O(2)—C(2)—C(3)	109·3 (2)	O(5)—C(5)—C(6)	108·5 (3)
C(1)—C(2)—C(3)	108·2 (2)	C(4)—C(5)—C(6)	113·6 (3)
O(3)—C(3)—C(2)	109·4 (2)	O(6)—C(6)—C(5)	112·2 (3)
O(3)—C(3)—C(4)	108·6 (2)		

C(1)—O(5)—C(5)—C(4)	62·0 (3)	C(2)—C(3)—C(4)—O(4)	−179·7 (2)
C(1)—O(5)—C(5)—C(6)	−174·6 (3)	C(2)—C(3)—C(4)—C(5)	57·0 (3)
C(5)—O(5)—C(1)—O(1)	171·4 (3)	O(4)—C(4)—C(5)—C(6)	58·4 (4)
C(5)—O(5)—C(1)—C(2)	−65·1 (3)	C(3)—C(4)—C(5)—O(5)	−57·3 (3)
O(5)—C(1)—C(2)—O(2)	−177·7 (2)	O(4)—C(4)—C(5)—O(5)	178·7 (2)
O(1)—C(1)—C(2)—O(2)	−58·7 (3)	C(3)—C(4)—C(5)—C(6)	−177·6 (3)
O(1)—C(1)—C(2)—C(3)	−179·3 (2)	C(4)—C(5)—C(6)—O(6)	44·6 (4)
O(5)—C(1)—C(2)—C(3)	61·6 (3)	O(5)—C(5)—C(6)—O(6)	−75·3 (4)
C(1)—C(2)—C(3)—O(3)	60·3 (3)	H(O1)—O(1)—C(1)—H(C1)	−167 (5)
C(1)—C(2)—C(3)—C(4)	−58·0 (3)	H(O2)—O(2)—C(2)—H(C2)	−52 (4)
O(2)—C(2)—C(3)—O(3)	−62·3 (3)	H(O3)—O(3)—C(3)—H(C3)	−5 (3)
O(2)—C(2)—C(3)—C(4)	179·5 (2)	H(O4)—O(4)—C(4)—H(C4)	−167 (4)
O(3)—C(3)—C(4)—O(4)	61·5 (3)	H(O6)—O(6)—C(6)—H(C6)	−121 (4)
O(3)—C(3)—C(4)—C(5)	−61·7 (3)		

in good agreement with the average values of these quantities observed in β-pyranoses (1·389 Å, 107·3°; Arnott & Scott, 1972) and with trends of these geometries predicted by theoretical calculations (Jeffrey, Pople & Radom, 1974).

The pyranose ring has a regular $^4C_1$ chair conformation as follows from the endocyclic torsion angles which are close to $\pm 60°$ and the puckering parameters of $Q = 0·611$ (3) Å, $\theta = 3·0$ (3)° and $\varphi = 71$ (5)° (Cremer & Pople, 1975). The exocyclic dihedral angles have values that are close to ideal *gauche* or *trans* conformations, except those involved in the hydroxymethyl group, where C(4)—C(5)—C(6)—O(6) is smaller [44·6 (4)°] than O(5)—C(5)—C(6)—O(6) [−75·3 (3)°]. This trend has been observed frequently as is shown by a statistical analysis of Marchessault & Pérez (1979). The torsion angles of the hydroxyl groups cover the whole range between 0 and 180°. This is commonly observed in saccharide structures and recently it has been confirmed by molecular-mechanics calculations (Kroon-Batenburg & Kanters, 1983) that the actual angles are mainly determined by intermolecular hydrogen bonding.

The hydrogen bonds are listed in Table 3. All five hydroxyl groups serve as proton donors in intermolecular hydrogen bonds; O(6)—H is involved in an unsymmetrical bifurcated hydrogen bond. O(3), which is axially positioned at the ring, is the only O atom that does not act as an acceptor. Anomeric O(1) is twice an acceptor, of a weak bond [H···O 2·45 (5) Å] and a

Table 3. *Hydrogen-bond distances* (Å) *and angles* (°) *of β-D-allose*

Bond No.	O–H···O	O–H	H···O	H···O*	O···O	O–H···O	Symmetry operation†
1	O(1)–H(O1)···O(4')	0·97 (7)	1·69 (7)	1·70	2·635 (3)	165 (6)	564·4
2	O(2)–H(O2)···O(6')	0·88 (5)	1·99 (5)	1·91	2·838 (4)	164 (4)	564·4
3	O(3)–H(O3)···O(2')	0·87 (4)	1·96 (4)	1·88	2·811 (3)	164 (4)	566·2
4	O(4)–H(O4)···O(1')	0·86 (5)	1·96 (5)	1·87	2·728 (3)	149 (4)	665·4
5	O(6)–H(O6)···O(1')	0·85 (5)	2·45 (5)	2·38	3·074 (3)	130 (4)	456·2
6	O(6)–H(O6)···O(5')	0·85 (5)	2·15 (5)	2·05	2·996 (3)	171 (5)	456·2
1a	O(4)···H(O1'')–O(1'')						565·4
2a	O(6)···H(O2'')–O(2'')						565·4
3a	O(2)···H(O3'')–O(3'')						466·2
4a	O(1)···H(O4'')–O(4'')						664·4
5a	O(1)···H(O6'')–O(6'')						556·2
6a	O(5)···H(O6'')–O(6'')						556·2

* Corrected by expanding the covalent O–H bond distances to the neutron diffraction value of 0·96 Å in the direction of the bond.

† The symmetry operation is performed on the O' (acceptors) and O'' (donors). The first three digits specify the lattice translations. The last digit indicates one of the following symmetry operations: (1) x, y, z; (2) $\frac{1}{2}+x, \frac{1}{2}-y, -z$; (3) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (4) $\frac{1}{2}-x, -y, \frac{1}{2}+z$ (*e.g.* 564·4 is +b and $-c$ from 555·4).
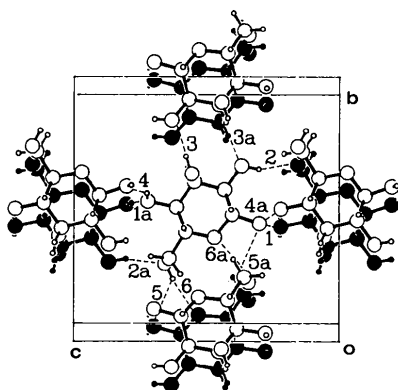

Fig. 2. Packing diagram viewed approximately down **a**. The hydrogen bonds are indicated by dashed lines and labelled according to Table 3. The central molecule corresponds to the symmetry operation 555·1.

strong bond [H···O 1·96 (5) Å] respectively, which is very unexpected since the anomeric oxygen rarely acts as an acceptor in crystal structures (Jeffrey & Takagi, 1978). This poor acceptor capacity was confirmed by model calculations (Tse & Newton, 1977) in which it was shown that the anomeric effect causes a depletion of charge at the anomeric proton. However, this depletion improves the donor quality of anomeric OH which is brought out by the presence of strong, short hydrogen bonds involving this OH group in crystal structures (Jeffrey & Takagi, 1978). In fact in β-D-allose the O(1)–H···O(4) bond has extremely short contacts [O···O 2·635 (3) and H···O 1·69 (7) Å].

The hydrogen-bonding scheme is shown in Fig. 2 and consists of an infinite chain ..O(4)–H···O(1)–H···O(4).. which propagates along **a** and a branch starting at O(3) and arriving *via* O(2) and O(6) at O(1), also propagating along **a**. Every β-D-allose molecule is surrounded by

eight symmetry-related molecules through hydrogen bonding. There are two short C–H···O contacts: one to axial O(3) [C(4)···O(3) 3·385 (4), H(4)···O(3) 2·60 (3) Å] and one to O(6) [C(5)···O(6) 3·420 (4), H(5)···O(6) 2·52 (4) Å] both in the **a** direction.

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