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 α,β -Trehalose Monohydrate

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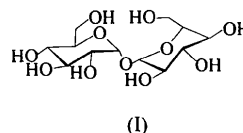
Abstract

The structure of α,β -trehalose (α -D-glucopyranosyl- β -D-glucopyranoside) monohydrate, C₁₂H₂₂O₁₁·H₂O, was determined in order to compare it with the molecular structures of the stereoisomers α,α -trehalose and β,β -trehalose. Both hexopyranosyl rings have ⁴C₁ conformations. In the glycosidic linkage, the torsion angles about the α -anomeric C—O bond are close to those observed in α,α -trehalose, but the torsion angles about the β -anomeric C—O bond deviate from those in β,β -trehalose and other β -pyranosides. This conformation is stabilized by an intramolecular hydrogen bond between the O(6) hydroxyl groups of the two glucopyranosyl residues. The hydrogen-bond system in the crystal structure consists of infinite and finite chains cross-linked by the water molecule.

Comment

α,β -Trehalose is one of the three stereoisomers about the 1–1 glycosidic linkage of the non-reducing disaccha-

ride consisting of two D-glucopyranosyl residues. α,α -Trehalose is widely distributed in nature (Birch, 1963), while α,β - and β,β -trehaloses are its synthetic isomers (Fischer & Delbrück, 1909; Helferich & Weis, 1956). α,α -Trehalose is attracting a great deal of attention as an efficient protecting agent for maintaining the structural integrity of the cytoplasm (Wiemken, 1990), and its structure has been extensively studied. The crystal structures of α,α -trehalose dihydrate (Brown *et al.*, 1972; Taga, Senma & Osaki, 1972), anhydrous α,α -trehalose (Jeffrey & Nanni, 1985), α,α -trehalose calcium bromide monohydrate (Cook & Bugg, 1973) and several α,α -trehalose derivatives (Williams, Lavalley, Hanssian & Brisse, 1979; Lee, Koh, Xu & Linden, 1994; Linden & Lee, 1994, 1995) have been reported so far. Little has been reported of the synthetic isomers, only the crystal structure of β,β -trehalose tetrahydrate (Lee & Koh, 1993) having been published previously. The β,β -trehalose molecule has exact C₂ symmetry in the crystal structure, while the title α,β -trehalose, (I), has an asymmetric configuration about the glycosidic linkage. The object of this study was to compare the molecular structure of asymmetric α,β -trehalose with the structures of other symmetric isomers.



A perspective view of the molecular structure of (I) is given in Fig. 1. Both glucopyranosyl rings adopt chair ⁴C₁ conformations denoted by the Cremer & Pople (1975) puckering parameters $Q = 0.53 \text{ \AA}$ and $\theta = 7.1^\circ$ for the α -pyranosyl ring, and $Q = 0.59 \text{ \AA}$ and $\theta = 5.8^\circ$ for the β -pyranosyl ring. The torsion angles about the glycosidic C(1)—O(1) bond [O(5)—C(1)—O(1)—C(1')] 68.8(6) and C(2)—C(1)—O(1)—C(1') $-169.3(4)^\circ$

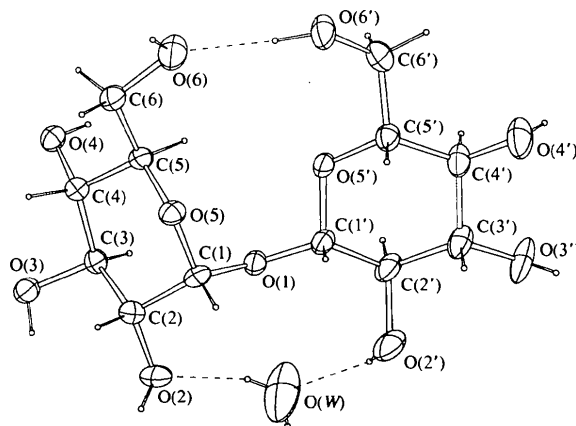


Fig. 1. The structure of α,β -trehalose monohydrate showing 50% probability displacement ellipsoids.

are close to those observed in α,α -trehalose. These angles describe the preferred *gauche-trans* conformations which are usually found for α -pyranosides. On the other hand, the torsion angles about the O(1)—C(1') bond [C(1)—O(1)—C(1')—O(5') $-93.4(7)$ and C(1)—O(1)—C(1')—C(2') $148.9(5)^\circ$] show considerable differences from those of β,β -trehalose. These angles deviate by $\sim 20^\circ$ from the stable conformations that were observed in several methyl β -pyranose sugars (Jeffrey & Takagi, 1977). In this conformation, however, repulsive interaction between the lone-pair electrons of the two ring O atoms of the molecule is small. The O(6) hydroxyl groups in both glucopyranosyl rings are oriented *gauche-trans*. The conformations are stabilized by an intramolecular hydrogen bond between the O(6) and O(6') hydroxyl groups.

Bond lengths and angles are within the expected ranges and agree well with the corresponding values in α,α -trehalose and β,β -trehalose. The glycosidic C(1)—O(1)—C(1') bond angle of $113.7(6)^\circ$ is comparable to those of α,α -trehalose (113.3 – 115.8°) and β,β -trehalose (115.2°). The bond lengths and angles associated with the anomeric C atoms and the ring O atoms show characteristic trends similar to those observed for crystalline α - and β -aldopyranosides (Takagi & Jeffrey, 1979).

The water molecule forms hydrogen bonds to the O(2) and O(2') hydroxyl groups of the same molecule. The hydrogen-bond system in the crystal structure consists of infinite and finite chains branched at the water molecules, and it is described by the diagrammatic schemes —O(2')—O(W)—O(2)—O(3')—O(3)—O(6')—O(6)— for the infinite chain, and >O(W)—O(4')—O(4)—O(5) for the finite chain.

Experimental

The title compound was obtained from Hayashibara Co. Ltd.

Crystal data

C₁₂H₂₂O₁₁·H₂O

$M_r = 360.314$

Monoclinic

$P2_1$

$a = 9.770(3) \text{ \AA}$

$b = 8.575(5) \text{ \AA}$

$c = 10.096(2) \text{ \AA}$

$\beta = 111.68(2)^\circ$

$V = 786.0(5) \text{ \AA}^3$

$Z = 2$

$D_x = 1.5224 \text{ Mg m}^{-3}$

$D_m = 1.515 \text{ Mg m}^{-3}$

D_m measured by flotation in cyclohexane/CCl₄

Data collection

Rigaku AFC-5 diffractometer

Mo K α radiation

$\lambda = 0.7107 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 8.75$ – 12.85°

$\mu = 0.138 \text{ mm}^{-1}$

$T = 295.0 \text{ K}$

Prism

$0.50 \times 0.50 \times 0.30 \text{ mm}$

Colourless

$R_{\text{int}} = 0.007$

$\theta_{\text{max}} = 25^\circ$

$\theta/2\theta$ scans

Absorption correction: none

1582 measured reflections

1484 independent reflections

1456 reflections with

$F > 3\sigma(F)$

Refinement

Refinement on F

$R = 0.041$

$wR = 0.049$

$S = 1.00$

1456 reflections

289 parameters

Only coordinates of H atoms refined, all from D map

$h = 0 \rightarrow 11$

$k = 0 \rightarrow 9$

$l = -11 \rightarrow 11$

3 standard reflections

every 150 reflections

intensity decay: 2%

$w = 1/[\sigma^2(F) + 0.023F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.24$

$\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.29 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Geometric parameters (\AA , $^\circ$)

C(1)—C(2)	1.515 (5)	O(1)—C(1')	1.402 (4)
C(1)—O(1)	1.41 (1)	C(1')—C(2')	1.525 (8)
C(1)—O(5)	1.416 (6)	C(1')—O(5')	1.419 (7)
C(2)—C(3)	1.51 (1)	C(2')—C(3')	1.520 (5)
C(2)—O(2)	1.414 (6)	C(2')—O(2')	1.430 (7)
C(3)—C(4)	1.524 (7)	C(3')—C(4')	1.526 (8)
C(3)—O(3)	1.422 (5)	C(3')—O(3')	1.430 (8)
C(4)—C(5)	1.525 (6)	C(4')—C(5')	1.519 (8)
C(4)—O(4)	1.43 (1)	C(4')—O(4')	1.418 (6)
C(5)—C(6)	1.511 (7)	C(5')—C(6')	1.503 (8)
C(5)—O(5)	1.44 (1)	C(5')—O(5')	1.429 (5)
C(6)—O(6)	1.410 (5)	C(6')—O(6')	1.424 (8)
C(2)—C(1)—O(1)	109.3 (6)	O(1)—C(1')—C(2')	109.4 (5)
C(2)—C(1)—O(5)	109.5 (3)	O(1)—C(1')—O(5')	107.3 (4)
O(1)—C(1)—O(5)	112.6 (5)	C(2')—C(1')—O(5')	108.6 (6)
C(1)—C(2)—C(3)	111.6 (5)	C(1')—C(2')—C(3')	107.8 (5)
C(1)—C(2)—O(2)	110.8 (3)	C(1')—C(2')—O(2')	110.1 (6)
C(3)—C(2)—O(2)	108.6 (6)	C(3')—C(2')—O(2')	108.1 (4)
C(2)—C(3)—C(4)	110.8 (5)	C(2')—C(3')—C(4')	110.6 (4)
C(2)—C(3)—O(3)	110.5 (6)	C(2')—C(3')—O(3')	109.3 (5)
C(4)—C(3)—O(3)	106.5 (3)	C(4')—C(3')—O(3')	109.0 (5)
C(3)—C(4)—C(5)	113.3 (3)	C(3')—C(4')—C(5')	110.5 (5)
C(3)—C(4)—O(4)	110.6 (6)	C(3')—C(4')—O(4')	110.9 (4)
C(5)—C(4)—O(4)	110.4 (5)	C(5')—C(4')—O(4')	106.6 (5)
C(4)—C(5)—C(6)	110.0 (3)	C(4')—C(5')—C(6')	111.5 (6)
C(4)—C(5)—O(5)	110.8 (5)	C(4')—C(5')—O(5')	109.7 (5)
C(6)—C(5)—O(5)	107.3 (6)	C(6')—C(5')—O(5')	106.8 (4)
C(5)—C(6)—O(6)	111.4 (3)	C(5')—C(6')—O(6')	112.9 (6)
C(1)—O(1)—C(1')	113.7 (6)	C(1')—O(5')—C(5')	112.2 (4)
C(1)—O(5)—C(5)	115.1 (6)		
C(1)—C(2)—C(3)—C(4)	−51.1 (6)		
C(1)—O(1)—C(1')—C(2')	148.9 (5)		
C(1)—O(1)—C(1')—O(5')	−93.4 (7)		
C(2)—C(1)—O(1)—C(1')	−169.3 (4)		
C(2)—C(1)—O(5)—C(5)	−61.0 (8)		
C(2)—C(3)—C(4)—C(5)	46.7 (8)		
C(3)—C(4)—C(5)—C(6)	−166.2 (7)		
C(3)—C(4)—C(5)—O(5)	−47.8 (9)		
C(4)—C(5)—C(6)—O(6)	−161.1 (7)		
C(4)—C(5)—O(5)—C(1)	56.2 (6)		
C(6)—C(5)—O(5)—C(1)	176.3 (4)		
O(1)—C(1)—C(2)—C(3)	−66.4 (6)		
O(1)—C(1)—O(5)—C(5)	60.9 (5)		
O(1)—C(1')—C(2')—C(3')	178.3 (6)		
O(1)—C(1')—O(5')—C(5')	175.3 (7)		
O(5)—C(1)—C(2)—C(3)	57.5 (8)		
O(5)—C(1)—O(1)—C(1')	68.8 (6)		
O(5)—C(5)—C(6)—O(6)	78.4 (7)		
C(1')—C(2')—C(3')—C(4')	−55.5 (8)		
C(2')—C(1')—O(5')—C(5')	−66.5 (8)		
C(2')—C(3')—C(4')—C(5')	52.5 (8)		
C(3')—C(4')—C(5')—C(6')	−172.0 (5)		
C(3')—C(4')—C(5')—O(5')	−53.9 (8)		

C(4')—C(5')—C(6')—O(6')	−167.9 (5)
C(4')—C(5')—O(5')—C(1')	62.3 (9)
C(6')—C(5')—O(5')—C(1')	−176.7 (6)
O(5')—C(1')—C(2')—C(3')	61.4 (7)
O(5')—C(5')—C(6')—O(6')	72.3 (7)

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

D—H...A	H...A	D...A	D—H...A
O(2)—H(O2)...O(3 ⁱ)	1.89 (4)	2.68 (1)	163 (2)
O(3)—H(O3)...O(6 ⁱⁱ)	1.87 (7)	2.682 (5)	167 (2)
O(4)—H(O4)...O(5 ⁱⁱⁱ)	2.06 (5)	2.812 (8)	146 (2)
O(6)—H(O6)...O(2 ^{iv})	2.07 (7)	2.831 (5)	155 (2)
O(2')—H(O2')...O(W)	1.95 (8)	2.699 (7)	153 (2)
O(3')—H(O3')...O(3 ^v)	1.91 (5)	2.705 (6)	170 (6)
O(4')—H(O4')...O(4 ^v)	1.91 (8)	2.660 (5)	154 (5)
O(6')—H(O6')...O(6)	1.91 (5)	2.728 (4)	154 (6)
O(W)—H(1W)...O(1)	1.96 (6)	2.76 (1)	169 (6)
O(W)—H(2W)...O(4 ⁱⁱ)	2.09 (9)	3.008 (6)	168 (6)

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

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *MSCIAFC Diffractometer Control Software*. Program(s) used to solve structure: *MULTAN88* (Main *et al.*, 1988). Program(s) used to refine structure: *KPPXRAY ORFLS* (Taga, Masuda, Higashi & Iizuka, 1991). Molecular graphics: *KPPXRAY*. Software used to prepare material for publication: *EDCIF-J* (Osaki & Taga, 1993).

Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: KH1115). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(6S)-8-C-Chloro-6,7,8-trideoxy-1,2:3,4-di-O-isopropylidene- α -D-galacto-octa-6,7-dieno-pyranose

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Abstract

The title structure, C₁₄H₁₉ClO₅, consists of an allene substituted with a Cl atom at one end joined at the other end to a D-galactopyranose ring bearing two fused isopropylidene groups.

Comment

One aspect of our research (Horton & Liu, 1996) is the investigation of stereospecific conversions of D-galactose-derived propargylic alcohols into chiral haloallenes. This can be accomplished by reacting suitable alcohols with SOCl₂/pyridine in boiling 1,4-dioxane. These reactions can afford either two stereoisomers [(2) and (3) as shown in the scheme] or possibly diastereomeric mixtures. These compounds differ in the arrangement of the Cl atom on the allene moiety. In the specific dehydration reaction depicted in the scheme below (Horton & Liu, 1996), only one product was obtained and the single-crystal structure was determined as a means of establishing the arrangement of ligands around the allene group. Our results here establish that the compound synthesized has the arrangement depicted as compound (2).

