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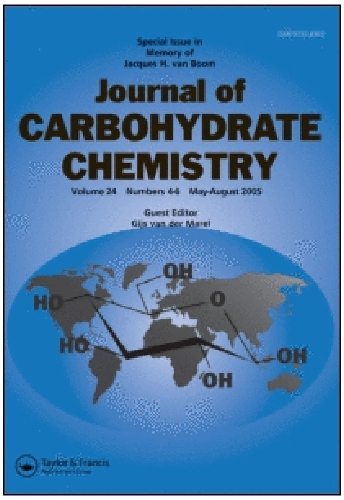

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Structure and Taste of 4,4'-Dideoxy-α,α-xylotrehalose[1]

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STRUCTURE AND TASTE OF 4,4'-DIDEOXY-α,α-XYLOTREHALOSE[1]

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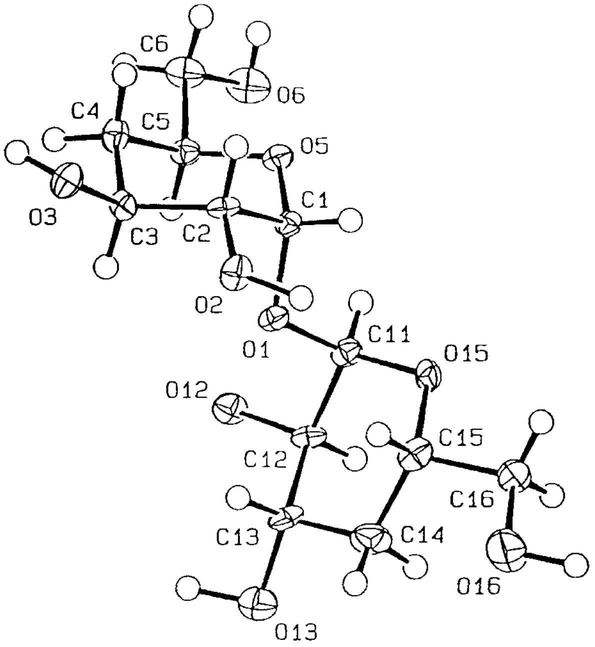
ABSTRACT

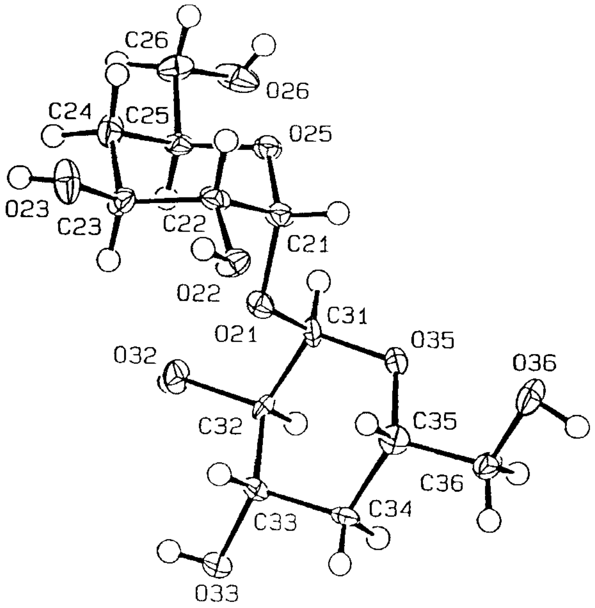
The X-ray structure of 4,4'-dideoxy-α,α-xylotrehalose is reported. The two symmetry independent molecules in the asymmetric unit differ significantly in the orientation of the hydroxymethyl groups. There is also a twist of ~19° about the anomeric linkage in molecule B. The pyranose rings have slightly distorted $^4C_1$ conformations. As observed for α,α-trehalose, the two pyranose residues are not exactly related by a twofold axis of symmetry through the O(1) atom. The X-ray data show that O(3) is optimally positioned to function as B in the Shallenberger AH,B system, with O(2) acting as AH, therefore explaining why the compound is nearly as sweet as the parent sugar.

INTRODUCTION

α,α-Trehalose is an ideal sugar for taste-structure studies[2] because the molecule contains two chemically equivalent D-glucopyranose residues in the most stable $^4C_1$ conformation, linked through their anomeric centre, and the sugar and its derivatives are all extremely stable.[3] The sweetness and structure relationships of a series of deoxy derivatives of α,α-trehalose and methyl α-D-glucopyranoside have been extensively



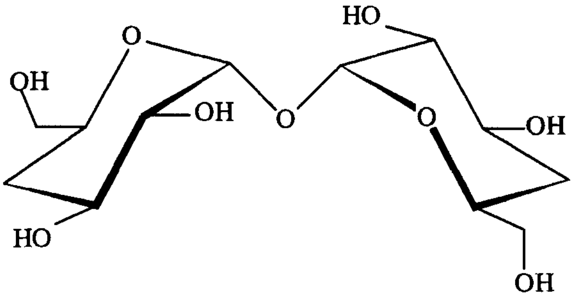
Molecule A



Molecule B

Fig. 1. ORTEP drawing of **1**

investigated[4] and it was found that the removal of the hydroxyl group at C(3) resulted in a significant drop in sweetness, whereas the removal of the hydroxyl group at any of the other positions had little or no effect on the sweet taste. We have shown[5] that 3,3-dideoxy-α,α-arabinotrehalose lacks sweetness because of the absence of the Shallenberger AH,B glucophore[6]. We now report the X-ray structure of 4,4'-dideoxy-α,α-xylotrehalose[7] (4-deoxy-α-D-xylohexopyranosyl 4-deoxy-α-D-xylohexopyranoside) (**1**).



(**1**) 4,4'-Dideoxy-α,α-xylotrehalose

RESULTS AND DISCUSSION

The two symmetry-independent molecules of **1** are shown in Fig. 1. These figures also depict the correct absolute configuration of the molecule as established by the synthesis of the compound. The atomic coordinates of the non-H atoms for the two symmetry-independent molecules are given in Table 1. Bond lengths, angles and selected torsion angles are given in Tables 2, 3 and 4, respectively.

The two molecules have very similar molecular dimensions except for the orientation of the hydroxymethyl group, which in molecule B, is rotated nearly 110° about the C(15)-C(16) bond when compared with molecule A. There is also a twist of approximately 19° about the anomeric linkage in molecule B. There appears to be some differences between the orientations of the H-atoms of some hydroxyl groups, although the positions of these atoms are not necessarily unambiguously known (see Experimental).

The two hexopyranosyl residues of both molecules have approximate C_2 symmetry. As observed for α,α-trehalose[8] and its derivatives,[5,9] the hydroxymethyl groups show the largest conformational difference between the two hexopyranosyl residues in one of the molecules. The torsion angles about the C(5)-C(6) bond in one of the rings of molecule A [O(15)-C(15)-C(16)-O(16) = 178.4(5)°, O(16)-C(16)-C(15)-C(14) = -60.6(7)°]

TABLE 1. Fractional atomic coordinates and equivalent isotropic temperature factors (Å) (with e.s.d.s in parentheses).

Molecule A					Molecule B				
Atom	x	y	z	U_{eq}*	Atom	x	y	z	U_{eq}*
O(1)	0.4132(4)	-0.0347(4)	0.01418(5)	0.018(1)	O(21)	0.3957(4)	0.4678(4)	0.12769(6)	0.017(1)
O(2)	0.6726(5)	0.0931(5)	0.00459(6)	0.022(1)	O(22)	0.5499(5)	0.2216(5)	0.12398(5)	0.022(1)
O(3)	0.6767(5)	0.0325(5)	-0.03989(6)	0.023(1)	O(23)	0.3850(5)	0.0640(5)	0.15271(7)	0.030(2)
O(5)	0.5013(5)	-0.2534(4)	0.00346(5)	0.019(1)	O(25)	0.4687(4)	0.4861(5)	0.16398(5)	0.018(1)
O(6)	0.3301(5)	-0.4845(5)	-0.01012(7)	0.031(2)	O(26)	0.3205(5)	0.6475(5)	0.19515(6)	0.032(2)
O(12)	0.1258(5)	-0.0583(5)	0.00898(6)	0.022(1)	O(32)	0.1239(5)	0.5688(5)	0.12812(6)	0.022(1)
O(13)	0.0607(5)	0.2156(5)	0.02960(7)	0.033(2)	O(33)	0.0942(5)	0.5937(5)	0.08135(6)	0.027(2)
O(15)	0.3869(4)	-0.0430(4)	0.05205(5)	0.019(1)	O(35)	0.4781(5)	0.6745(4)	0.11135(5)	0.018(1)
O(16)	0.4601(7)	0.2665(5)	0.08290(7)	0.045(2)	O(36)	0.7274(5)	0.6688(5)	0.08609(6)	0.027(2)
C(1)	0.5359(7)	-0.1186(6)	0.01124(8)	0.015(2)	C(21)	0.5011(7)	0.4329(7)	0.14337(8)	0.019(2)
C(2)	0.6336(6)	-0.0405(7)	-0.00363(8)	0.017(2)	C(22)	0.5072(7)	0.2716(7)	0.14441(8)	0.019(2)
C(3)	0.5710(6)	-0.0302(7)	-0.02643(8)	0.016(2)	C(23)	0.3671(7)	0.2150(7)	0.15144(8)	0.019(2)
C(4)	0.5323(7)	-0.1764(7)	-0.03395(8)	0.021(2)	C(24)	0.3305(7)	0.2778(7)	0.17338(9)	0.023(2)
C(5)	0.4386(7)	-0.2539(6)	-0.01786(8)	0.017(2)	C(25)	0.3357(7)	0.4375(7)	0.17248(8)	0.018(2)
C(6)	0.4216(7)	-0.4068(7)	-0.0243(1)	0.024(2)	C(26)	0.3212(7)	0.4971(7)	0.19513(8)	0.023(2)
C(11)	0.3284(7)	-0.0779(7)	0.03206(8)	0.018(2)	C(31)	0.3729(7)	0.6135(7)	0.12463(8)	0.017(2)
C(12)	0.1835(7)	-0.0141(7)	0.02903(9)	0.018(2)	C(32)	0.2286(7)	0.6315(7)	0.11446(8)	0.016(2)
C(13)	0.1947(7)	0.1466(7)	0.03020(9)	0.021(2)	C(33)	0.2248(7)	0.5658(7)	0.09217(8)	0.020(2)
C(14)	0.2620(8)	0.1831(7)	0.0511(1)	0.029(2)	C(34)	0.3415(7)	0.6273(7)	0.07857(8)	0.022(2)
C(15)	0.3990(7)	0.1077(7)	0.05543(9)	0.022(2)	C(35)	0.4828(7)	0.6151(7)	0.08949(8)	0.020(2)
C(16)	0.4428(8)	0.1210(7)	0.07872(9)	0.026(2)	C(36)	0.5910(7)	0.6961(7)	0.07726(9)	0.023(2)

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Bond lengths (Å) and bond angles (°) (with e.s.d.s in parentheses).

Molecule A		Molecule B	
O(1)-C(1)	1.427(7)	O(21)-C(21)	1.436(7)
O(1)-C(11)	1.431(6)	O(21)-C(31)	1.417(7)
O(2)-C(2)	1.420(7)	O(22)-C(22)	1.412(6)
O(3)-C(3)	1.437(6)	O(23)-C(23)	1.450(7)
O(5)-C(1)	1.410(7)	O(25)-C(21)	1.408(6)
O(5)-C(5)	1.450(6)	O(25)-C(25)	1.448(7)
O(6)-C(6)	1.443(7)	O(26)-C(26)	1.432(8)
O(12)-C(12)	1.422(6)	O(32)-C(32)	1.437(6)
O(13)-C(13)	1.435(8)	O(33)-C(33)	1.438(7)
O(15)-C(11)	1.398(6)	O(35)-C(31)	1.420(7)
O(15)-C(15)	1.455(7)	O(35)-C(35)	1.469(6)
O(16)-C(16)	1.418(8)	O(36)-C(36)	1.432(7)
C(1)-C(2)	1.506(8)	C(21)-C(22)	1.539(9)
C(2)-C(3)	1.537(7)	C(22)-C(23)	1.503(9)
C(3)-C(4)	1.513(8)	C(23)-C(24)	1.526(8)
C(4)-C(5)	1.528(8)	C(24)-C(25)	1.522(9)
C(5)-C(6)	1.518(9)	C(25)-C(26)	1.521(7)
C(11)-C(12)	1.519(9)	C(31)-C(32)	1.521(8)
C(12)-C(13)	1.535(9)	C(32)-C(33)	1.517(7)
C(13)-C(14)	1.485(8)	C(33)-C(34)	1.513(8)
C(14)-C(15)	1.512(9)	C(34)-C(35)	1.511(8)
C(15)-C(16)	1.508(7)	C(35)-C(36)	1.493(8)

TABLE 3. Bond Angles (°) with e.s.d.'s in parentheses.

Molecule A		Molecule B	
C(1)-O(1)-C(11)	113.6(4)	C(21)-O(21)-C(31)	115.1(5)
C(1)-O(5)-C(5)	114.2(4)	C(21)-O(25)-C(25)	114.0(4)
C(11)-O(15)-C(15)	113.2(4)	C(31)-O(35)-C(35)	113.5(4)
O(1)-C(1)-O(5)	111.2(5)	O(21)-C(21)-O(25)	112.2(5)
O(1)-C(1)-C(2)	107.9(5)	O(21)-C(21)-C(22)	106.6(5)
O(5)-C(1)-C(2)	112.6(4)	O(25)-C(21)-C(22)	109.2(4)
O(2)-C(2)-C(1)	112.6(4)	O(22)-C(22)-C(21)	108.0(5)
O(2)-C(2)-C(3)	112.0(5)	O(22)-C(22)-C(23)	113.2(5)
C(1)-C(2)-C(3)	110.8(5)	C(21)-C(22)-C(23)	109.7(5)
O(3)-C(3)-C(2)	106.8(5)	O(23)-C(23)-C(22)	105.5(5)
O(3)-C(3)-C(4)	111.9(5)	O(23)-C(23)-C(24)	111.5(5)
C(2)-C(3)-C(4)	108.6(5)	C(22)-C(23)-C(24)	108.7(5)
C(3)-C(4)-C(5)	112.7(4)	C(23)-C(24)-C(25)	110.5(5)
O(5)-C(5)-C(4)	110.7(5)	O(25)-C(25)-C(24)	111.2(5)
O(5)-C(5)-C(6)	106.7(5)	O(25)-C(25)-C(26)	107.2(5)
C(4)-C(5)-C(6)	110.7(5)	C(24)-C(25)-C(26)	109.6(5)
O(6)-C(6)-C(5)	113.2(5)	O(26)-C(26)-C(25)	112.0(5)
O(1)-C(11)-O(15)	113.2(5)	O(21)-C(31)-O(35)	111.7(5)
O(1)-C(11)-C(12)	107.5(5)	O(21)-C(31)-C(32)	107.7(5)
O(15)-C(11)-C(12)	112.1(5)	O(35)-C(31)-C(32)	110.5(4)
O(12)-C(12)-C(11)	109.9(5)	O(32)-C(32)-C(31)	109.6(4)
O(12)-C(12)-C(13)	111.3(5)	O(32)-C(32)-C(33)	110.4(5)
C(11)-C(12)-C(13)	109.2(5)	C(31)-C(32)-C(33)	110.6(5)
O(13)-C(13)-C(12)	113.1(6)	O(33)-C(33)-C(32)	111.7(5)
O(13)-C(13)-C(14)	107.4(5)	O(33)-C(33)-C(34)	107.7(4)
C(12)-C(13)-C(14)	107.7(5)	C(32)-C(33)-C(34)	109.3(5)
C(13)-C(14)-C(15)	114.7(5)	C(33)-C(34)-C(35)	112.0(5)
O(15)-C(15)-C(14)	112.0(5)	O(35)-C(35)-C(34)	110.9(5)
O(15)-C(15)-C(16)	104.0(5)	O(35)-C(35)-C(36)	106.9(5)
C(14)-C(15)-C(16)	111.7(5)	C(34)-C(35)-C(36)	110.3(5)
O(16)-C(16)-C(15)	106.8(5)	O(36)-C(36)-C(35)	109.7(5)

describes the *trans-gauche* conformation. This conformation, which is generally forbidden for glucopyranosyl moieties[10] because of interaction between O(4) and O(6), was also found in 2,2',3,3'-tetra-*o*-acetyl-6,6'-dichloro-4,4',6,6'-dideoxy-α,α-trehalose.[9] This conformation can be adopted in these derivatives because of the absence of a substituent at C(4). The corresponding torsion angles for the other ring in molecule A and both rings in molecule B (Table 4) describe the *gauche-trans* arrangement.

All of the pyranose rings have slightly distorted ${}^4C_1$ conformations, with puckering parameters[11] given in Table 5. The distortion is towards the ${}^2E$ conformation as indicated by the φ_2 values (which are close to 120°). This flattening of the oxygen apex allows the ring C-O-C angle to widen to >113° in each of the pyranose rings. The two glycosidic-linkage torsion angles are nearly equal in molecule A [73.6(6)° and 71.4(5)°], compared with those of molecule B [59.6(6)° and 78.8(5)°]. The pyranose residues are,

TABLE 4. Selected Torsion Angles (°) with e.s.d.s in parentheses.

Molecule A		Molecule B	
Within the pyranose rings			
C(1)-C(2)-C(3)-C(4)	-53.3(7)	C(21)-C(22)-C(23)-C(24)	-58.2(6)
C(1)-O(5)-C(5)-C(4)	54.3(6)	C(21)-O(25)-C(25)-C(24)	56.9(6)
C(2)-C(1)-O(5)-C(5)	-56.9(6)	C(22)-C(21)-O(25)-C(25)	-59.7(6)
C(2)-C(3)-C(4)-C(5)	52.9(7)	C(22)-C(23)-C(24)-C(25)	54.9(7)
C(11)-C(12)-C(13)-C(14)	-55.7(6)	C(31)-C(32)-C(33)-C(34)	-55.1(7)
C(11)-O(15)-C(15)-C(14)	51.0(6)	C(31)-O(35)-C(35)-C(34)	56.0(7)
C(12)-C(11)-O(15)-C(15)	-57.9(6)	C(32)-C(31)-O(35)-C(35)	-58.3(6)
C(12)-C(13)-C(14)-C(15)	52.2(8)	C(32)-C(33)-C(34)-C(35)	53.5(7)
O(5)-C(1)-C(2)-C(3)	56.0(7)	O(25)-C(21)-C(22)-C(23)	60.4(6)
O(5)-C(5)-C(4)-C(3)	-53.0(7)	O(25)-C(25)-C(24)-C(23)	-53.0(7)
O(15)-C(11)-C(12)-C(13)	60.6(6)	O(35)-C(31)-C(32)-C(33)	57.9(6)
O(15)-C(15)-C(14)-C(13)	-49.6(7)	O(35)-C(35)-C(34)-C(33)	-53.1(7)
Outside the pyranose rings			
O(1)-C(1)-O(5)-C(5)	64.4(5)	O(21)-C(21)-O(25)-C(25)	58.3(6)
O(1)-C(1)-C(2)-O(2)	59.1(6)	O(21)-C(21)-C(22)-O(22)	62.8(6)
O(1)-C(1)-C(2)-C(3)	-67.2(6)	O(21)-C(21)-C(22)-C(23)	-61.0(5)
O(1)-C(11)-O(15)-C(15)	64.0(6)	O(21)-C(31)-O(35)-C(35)	61.6(6)
O(1)-C(11)-C(12)-O(12)	57.9(6)	O(21)-C(31)-C(32)-O(32)	57.6(6)
O(1)-C(11)-C(12)-C(13)	-64.5(6)	O(21)-C(31)-C(32)-C(33)	-64.4(6)
O(2)-C(2)-C(1)-O(5)	-177.8(4)	O(22)-C(22)-C(21)-O(25)	-175.8(5)
O(2)-C(2)-C(3)-O(3)	59.2(6)	O(22)-C(22)-C(23)-O(23)	61.4(6)
O(3)-C(3)-C(4)-C(5)	170.6(5)	O(23)-C(23)-C(24)-C(25)	170.7(5)
O(5)-C(1)-O(1)-C(11)	71.4(5)	O(25)-C(21)-O(21)-C(31)	59.6(6)
OO(5)-C(5)-C(6)-O(6)	61.5(7)	O(25)-C(25)-C(26)-O(26)	61.2(7)
O(6)-C(6)-C(5)-C(4)	-178.0(5)	O(26)-C(26)-C(25)-C(24)	-178.0(6)
O(12)-C(12)-C(13)-O(13)	64.2(6)	O(32)-C(32)-C(33)-O(33)	64.4(6)
O(12)-C(12)-C(13)-C(14)	-177.3(5)	O(32)-C(32)-C(33)-C(34)	-176.6(5)
O(13)-C(13)-C(14)-C(15)	174.3(5)	O(33)-C(33)-C(34)-C(35)	174.9(5)
O(15)-C(11)-O(1)-C(1)	73.6(6)	O(35)-C(31)-O(21)-C(21)	78.8(5)
O(15)-C(15)-C(16)-O(16)	178.4(5)	O(35)-C(35)-C(36)-O(36)	66.9(6)
O(16)-C(16)-C(15)-C(14)	-60.6(7)	O(36)-C(36)-C(35)-C(34)	-172.4(5)

TABLE 5. Puckering parameters for the pyranose rings of the two symmetry-independent molecules of **1**.

Molecule A			Molecule B		
	Ring 1	Ring 2		Ring 1	Ring 2
Q (Å)	0.541	0.546	Q (Å	0.576	0.557
q_2 (Å)	0.024	0.077	q_2(Å)	0.049	0.028
q_3 (Å)	0.541	0.541	q_3 (Å)	0.574	0.556
φ_2 (°)	148.7	113.7	φ_2 (°)	119.8	107.4
θ (°)	2.5	8.1	θ (°)	4.9	2.9

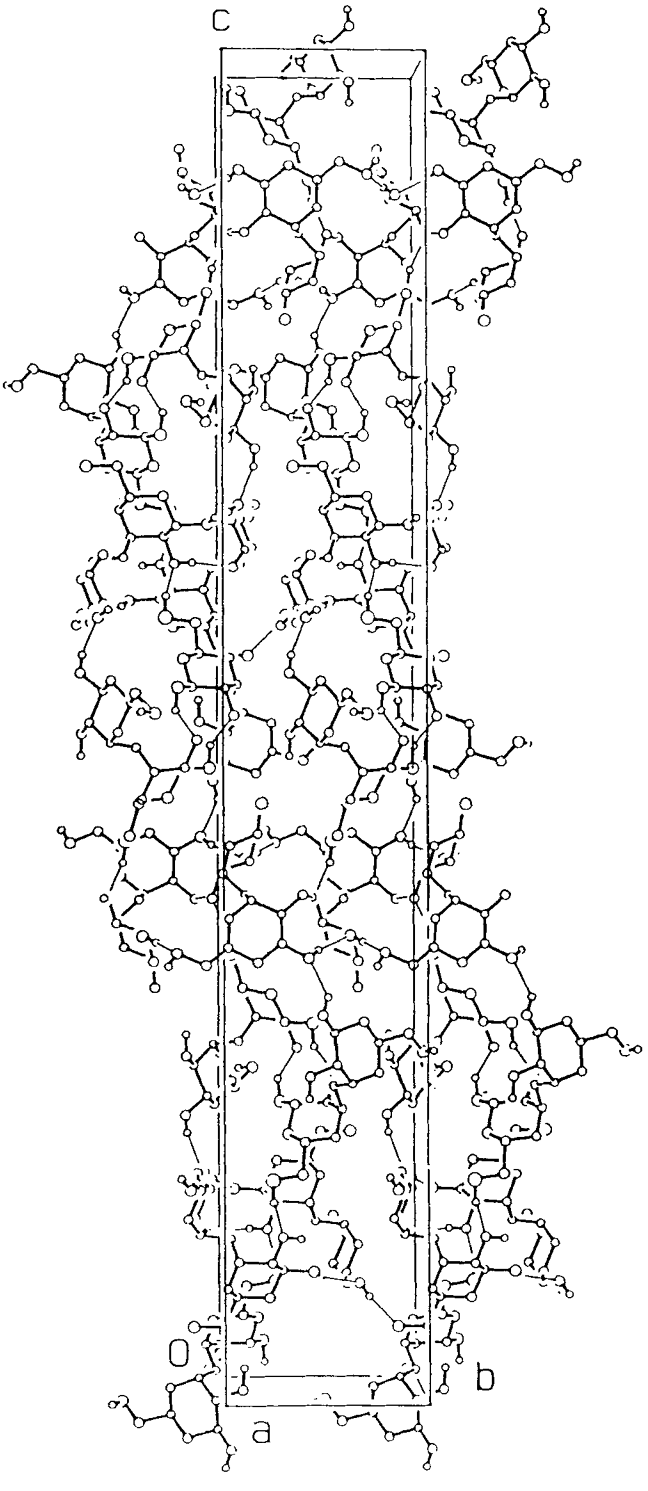


Fig. 2. Molecular packing of **1**, viewed down **a**, showing the hydrogen bonding interactions.

TABLE 6. Hydrogen-bonding distances (Å) and angles (°) in the crystal structure of 4,4'-dideoxy-α,α-xylotrehalose (1)

Hydrogen bond (or O...O) contact)	Symmetry Operations	Distances (Å)			Angle (°)
		O—H	O...O	H...O	O—H···O
O(3)-H...O(33')	[2,000]	0.87	2.752(5)	2.07	135
O(6)-H...O(6')	[2,1-10]	0.79	2.79(1)	2.17	135
O(13)-H...O(12')	[2,000]	1.04	2.780(6)	1.97	133
O(16)-H...O(22)	[1,000]	1.02	2.720(6)	1.74	160
O(22)-H...O(32')	[4,000]	0.86	2.855(6)	2.01	169
O(23)-H...O(36')	[4,-100]	0.73	2.765(6)	2.13	145
O(26)-H...O(3')	[3,010]	0.65	2.781(7)	2.21	148
O(32)-H...O(35')	[4,-110]	0.61	2.886(6)	2.32	156
O(33)-H...O(23')	[4,-100]	0.74	2.682(6)	1.95	167
O(36)-H...O(26')	[4,010]	0.83	2.756(6)	1.96	163
O(2)...O(12')	[2,100]		2.714(6)		
O(2)...O(6')	[2,100]		2.728(7)		
O(12)...O(12')	[2,000]		2.716(9)		

Symmetry operators: (1) x, y, z; (2) y, x, -z;
(3) 1/2+y, 1/2-x, 1/4+z; (4) 1/2+x, 1/2-y, 1/4-z

therefore, more symmetrically oriented about the glycosidic oxygen bond in molecule A than in molecule B.

The crystal structure of **1** is stabilized by a complex 3-dimensional network of intermolecular hydrogen bonds (Fig. 2 and Table 6). In molecule B, each hydroxyl group acts as a donor and an acceptor for one hydrogen bond. In addition, the ring oxygen atom, O(35), acts as an acceptor for a fairly weak interaction. All except three of the interactions are with other type B molecules.

The hydroxyl groups of molecule A are not "saturated" with hydrogen bonding interactions. O(16) and O(13) act as donors only. The interaction at O(12) is unclear because it was not possible to locate the hydrogen atom of this group. O(12) is clearly an acceptor of one hydrogen bond, but there are two additional O...O contacts close enough to be considered interactions. The angles around O(12) suggest that the interaction with O(2) probably has O(12) acting as the donor. The interaction at O(2) is also unclear, but it probably has an acceptor interaction with O(12) and a donor interaction with O(6), although the O-H(12)...O(6) distance is 2.74 Å. It is possible that O-H(12) is in the incorrect position, resulting from the poor data quality. O(6) clearly shows a donor and an acceptor interaction with itself from an adjacent molecule, but there is a third short O...O contact with O(2), presumably an acceptor interaction. The ring O-atoms of molecule A are not involved in any hydrogen bonding interactions. As observed for other trehalose compounds[5,8,9] there are no intramolecular hydrogen bonding interactions.

Systematic studies[4] on the taste of a series of deoxy derivatives of methyl α-D-glucopyranoside and α,α-trehalose indicated that whereas the removal of the C(3) hydroxyl group resulted in a total loss of sweetness, the removal of the other hydroxyl groups had little or no effect on the intensity of the sweetness. 3,3'-Dideoxy-α,α-arabinotrehalose was found[5] to be devoid of a Shallenberger AH,B glucophore and is therefore unable to bind to the corresponding AH,B system of the taste receptor. The X-ray data of **1** clearly show that, in both the symmetry-independent molecules, O(3) is 2.8-3.0 Å from O(2). This is the optimum AH-to-B distance[6] for sweetness, therefore confirming the unique importance of O(3) in eliciting the sweet taste response, acting as B in the Shallenberger AH,B system, with either the C(4) or, less commonly (as in **1**, when O(4) is absent), the C(2) hydroxyl group acting as AH.

The Kier[12] extension to the Shallenberger AH,B system is that a third lipophillic (γ) function is required to determine the intensity of the sweet taste response. The γ function is viewed as a function that facilitates the accession of a taste molecule to taste receptors and, in sugars, it has been proposed[13] to be located at an interatomic distance of ~3.1 Å from A and ~5.5 Å from B. Although its role in sugar molecules is minimal, it is of structural interest to modify the γ-effect. A methylene group should have the potential of performing as a γ function. In **1**, C(4) is, however, not ideally located to act as a γ function; it is ~3.7 Å from O(2) and ~2.4 Å from O(3).

EXPERIMENTAL

4,4'-Dideoxy-α,α-xylotrehalose (**1**) was prepared by the method described by Birch, Lee and Richardson[7]. Colourless prisms of **1** were grown by slow evaporation of solvent from an aqueous acetone solution at room temperature.

Crystal structure determination. Crystal data for $C_{12}H_{22}O_9$, M_r = 310.30, tetragonal $P4_32_12$ (#96), a = 9.518(1), c = 61.982(4) Å, V = 5616(2) Å^3, Z = 16, D_{calc} = 1.468 g cm^{-3}, λ(MoK_α) = 0.71069 Å, μ(MoK_α) = 1.185 cm^{-1}, F(000) = 2656, T = -100±1°C. The diffraction data were obtained from a single crystal of approximate dimensions 0.30 x 0.48 x 0.50 mounted on a glass fiber using a *Rigaku* AFC5R diffractometer with graphite-monochromated MoK_α radiation. The unit cell parameters were refined from the setting angles of 22 carefully centered reflections in the range 36° < 2θ < 40°. The space group was determined from systematic absences and a knowledge of the chirality of the molecules from the synthesis of the compound, which enable the elimination of the enantiomorphous space group $P4_12_12$. Intensities were collected using ω scans with a fixed scanning rate of 8° min^{-1} (up to 4 scans/reflection). The intensities of three reflections which were measured every 150 reflections remained stable throughout the data collection. Of the 4992 reflections which were collected with 2θ ≤

55°, 4562 were unique ($R_{int} = 0.078$), and 3493 with intensities $I > 3\sigma(I)$ were used for structure analysis.

The structure[13] was solved by direct methods[14] and refined by full-matrix least-squares method based on F. An empirical absorption correction[15] was applied (T_{max} = 1.177; T_{min} 0.803). All the hydrogen atoms, except those bonded to hydroxyl groups, were placed in geometrically calculated positions with a C-H distance of 0.95 Å. The hydrogen atoms of the hydroxyl groups were placed in the positions indicated by a difference electron density map, although some of the positions have poor distances and angles about the hydroxyl O-atom. One hydroxyl hydrogen atom could not be located and has been omitted from the final model. The positions of the hydrogen atoms were not refined and each hydrogen atom was assigned a fixed isotropic thermal factor ($1.2B_{eq}$ of the atom to which it was bonded). The weighting scheme used in the final stage was $w = [\sigma^2(F_o) + (0.005F_o)^2]^{-1}$. The refinement converged to give R = 0.074 and R_w = 0.076. All calculations were performed using the *TEXSAN*[16] crystallographic package. A list of structure factors is available from the second author.

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REFERENCES AND NOTES

1. Part 4 in the series "Structure of Trehalose Derivatives". For Part 3, see ref 9.

2. C. K. Lee, *Advan. Carbohydr. Chem. Biochem.*, **45**, 199 (1987).

3. C. K. Lee, In "*Developments in Food Carbohydrates*, Vol 2; C. K. Lee, Ed.; Applied Science Publishers, UK, 1980, pp 1-89.

4. G. G. Birch and C. K. Lee, *J. Food Sci.*, **39**, 947 (1974).

5. C. K. Lee and L. L. Koh, *Carbohydr. Res.*, In press.

6. R. S. Shallenberger and T. E. Acree, *Nature*, **216**, 480 (1967); R. S. Shallenberger and T. E. Acree, In "*Handbook of Sensory Physiology. IV"; Chemical Senses, 2; Taste*, Vol 4, L. M. Beidler, Ed.; Springer-Verlag, Berlin, 1971, pp 221-277.

7. G. G. Birch, C. K. Lee and A. C. Richardson, *Carbohydr. Res.*, **36**, 97 (1974).

8. G. M. Brown, D. C. Rohrer, B. Berking, C. A. Beevers, R. O. Gould and R. Simpson, *Acta Crystallogr.*, **B28**, 3145 (1972); T. Taka, M. Senma and K Osaki, *Acta Crystallogr.*, **B28**, 3258 (1972); G. A. Jeffrey and R. Nanni, *Carbohydr. Res.*, **137**, 21 (1985).

9. C. K. Lee, A. Linden, L. L. Koh and Y. Xu, Submitted for publication.

10. D. C. Fries, S. T. Rao and M. Sundaralingam, *Acta Crystallogr.*, **B27**, 994 (1971) .

11. D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 1354 (1975).

12. L. B. Kier, *J. Pharm. Sci.*, **61**, 1394 (1972).

13. The accuracy of the atomic parameters is not very high, as reflected in the final R-factors for the refinement. This is a result of the quality of the reflection data and it may be attributable to crystal quality, but is more likely a result of partial reflection overlap caused by the very long *c*-axis. An attempt was made to keep the scan width small in order to minimise overlap problems, but the broadness of the reflection profiles restricted the degree to which the scan width could be narrowed. Data was collected on three crystals, and the results from the best refinement have been used. All of the crystals were of similar quality, as demonstrated by the reflection profile.

14. G. M. Sheldrick, *SHELXS-86. Acta Crystallogr.* **A46**, 467 (1990).

15. N. Walker and D. Stewart, *Acta Crystallogr.* **A39**, 158 (1983).

16. *TEXSAN* - *TEXRAY* Single Crystal Structure Analysis Package, Version 5.0. Molecular Structure Corporation, The Woodlands, Texas (1989).