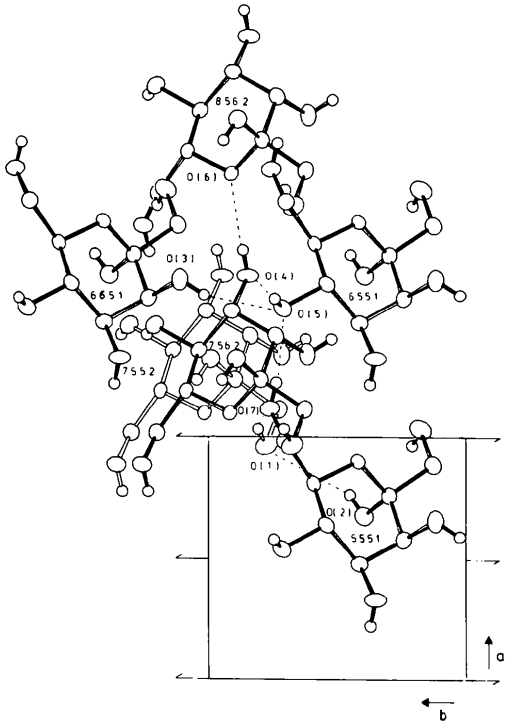

Fig. 2. Projection of the structure along *c*. The hydrogen bonds in the five-link chain with a single branch are indicated by dashed lines. The symmetry operations are defined in the footnote to Table 8. The aliphatic H atoms have been omitted.

an acceptor, which agrees with the above prediction, the donor–acceptor O(2)—H···O(1) contact of 1·95 Å is by no means indicative of a strong interaction. The donor-only O(3)—H···O(5) distance of 2·19 Å is much larger than the comparable bonds in monosaccharides (Jeffrey, Gress & Takagi, 1977), and together with the appreciable deviation of the O(3)—H···O(5) angle from linearity, this hydrogen-bond interaction must be considered as a very weak bond.

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The Crystal and Molecular Structure of 4-*O*-β-D-Glucopyranosyl-D-glucitol

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Abstract

4-*O*-β-D-Glucopyranosyl-D-glucitol, $C_{12}H_{24}O_{11}$, is orthorhombic, space group $P2_12_12_1$, with a = 5·295 (1), b = 7·770 (1), c = 35·514 (6) Å and Z = 4. The structure was solved by direct methods and refined to $R(F)$ = 0·033 for 1542 reflexions. The glucose ring has the $^4C_1$ chair conformation and the conformation of the primary alcohol group is *gauche–gauche*. The C-atom chain of the glucitol residue has the bent *Msc*, *ap*, *Psc* (*MAP*) conformation and differs from that observed in the *A* form of D-glucitol and in the D-glucitol–

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pyridine complex which both have the bent *MAA* conformation. The conformation of the terminal hydroxyl groups is *AA* in the glucitol residue and the *A* form of D-glucitol, and *MP* in the D-glucitol–pyridine complex. The hydrogen-bond pattern is very complicated in that three donors form bifurcated hydrogen bonds. Two hydrogen bonds are intramolecular.

Introduction

An important conformation-stabilizing factor of α- and β-(1→4)-linked glucopyranoside disaccharides is the intramolecular hydrogen bond which links the two pyranose residues (Sundaralingam, 1968). In α-maltose (Takusagawa & Jacobson, 1978) and β-maltose (Gress & Jeffrey, 1977), both having a 1*a*,4*e* glycosidic link, the intramolecular hydrogen bond involves two hydroxyl groups, whereas in 1*e*,4*e*-linked cellobiose (Chu & Jeffrey, 1968) the bond is between a hydroxyl group and a ring O atom. In disaccharides composed of different monosaccharides and derivatives like α-lactose (Fries, Rao & Sundaralingam, 1971), β-lactose (Hirotsu & Shimada, 1974), turanose (Kanters, Gaykema & Roelofsen, 1978), sucrose (Brown & Levy, 1973), methyl β-maltoside (Chu & Jeffrey, 1967) and phenyl α-maltoside (Tanaka, Tanaka, Ashida & Kakudo, 1976) the intramolecular hydrogen bond is also seen to play a dominant role in determining the conformation of the glycosidic link. In these compounds the formation of an intramolecular bond is facilitated by the rotational flexibility of the C—O—C bonds of the bridge.

In the class of hexosylhexitols, composed of an aldopyranose linked to a hexitol by a C—O—C bridge, the acyclic unfolded half of the molecule is much more flexible than the rigid pyranose ring. In order to study the effect of replacing a pyranose ring by a polyalcoholic side chain in a disaccharide on the conformation of the glycosidic link and intramolecular hydrogen bonding, the structure analysis of 4-*O*-β-D-glucopyranosyl-D-glucitol was undertaken. This hexosylhexitol is derived from the disaccharide β-cellobiose and can be obtained by reductive ring opening of its reducing pyranose ring. Recently Takagi & Jeffrey (1977*a*) reported the structure of the first member of the class of hexosylpentitols, 4-*O*-β-D-galactopyranosyl-L-rhamnitol, and showed the presence of an intramolecular hydrogen bond linking a terminal rhamnitol hydroxyl group to the galactose ring O atom.

Experimental

The title compound was provided by Dr J. F. G. Vliegenthart of the Organic Chemistry Laboratory of the University of Utrecht. Crystals were grown from an aqueous methanolic solution at room temperature. Photographs showed that the crystal system is orthorhombic with space group $P2_12_12_1$. Accurate cell dimensions and intensities were measured on an automatic Nonius CAD-4 diffractometer with Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) and the ω–2θ scan technique. The crystal data are summarized in Table 1. 1542 independent intensities were collected up to $\sin\theta/\lambda = 0.60$ Å^{-1} of which 513 with $I < 2.5\sigma(I)$ were considered unobserved. The intensity data were corrected for Lorentz–polarization and absorption (Coppens, 1970).

Structure determination and refinement

The structure was solved with the *MULTAN* system (Main, Lessinger, Woolfson, Germain & Declercq, 1974) using 300 normalized structure factors with $|E| > 1.30$. The first E map revealed all nonhydrogen atoms. After block-diagonal least-squares refinement with anisotropic thermal parameters, a difference map showed all 24 H atoms with electron densities ranging from 0.27 to 0.59 e Å^{-3}. The positional parameters of the H atoms, with constant isotropic thermal parameters equal to those of the carrier atoms, were included in the refinement. Full-matrix refinement gave a final $R = \sum||F_o| - |F_c||/|F_o| = 0.033$ and $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2} = 0.019$. The quantity minimized was $\sum w(F_o - F_c)^2$ with weights $w = \sigma^{-2}(F_o)$. In the last stage of the refinement an isotropic correction for secondary extinction was applied (Larson, 1967). The final value of g was 2.8×10^{-3}, the goodness of fit was 1.69, and the average shift/error for all parameters was 0.016. A final difference synthesis showed no peaks above 0.21 e Å^{-3}. Scattering factors for C and O were taken from Cromer & Mann (1968) and for H from Stewart, Davidson & Simpson (1965). Positional parameters are listed in Tables 2 and 3.* Refinement and subsequent calculations were performed with the XRAY system (Stewart, 1976).

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34212 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Crystal data for* 4-*O*-β-D-*glucopyranosyl*-D-*glucitol*

Molecular formula	$C_{12}H_{24}O_{11}$	Space group	$P2_12_12_1$
Formula weight	344.3	V (Å^3)	1461.2
Crystal system	Orthorhombic	Z	4
a (Å)	5.295 (1)	D_x (Mg m^{-3})	1.564
b (Å)	7.770 (1)	μ(Mo $K\alpha$) (mm^{-1})	0.1504
c (Å)	35.514 (6)	λ(Mo $K\alpha$) (Å)	0.71069
Systematic absences	$h00$, $h = 2n + 1$ $0k0$, $k = 2n + 1$ $00l$, $l = 2n + 1$	Crystal dimensions (mm)	0.39 × 0.24 × 0.06

Table 2. *Fractional atomic coordinates* ($\times 10^5$) *of the* C *and* O *atoms in* 4-*O*-β-D-*glucopyranosyl*-D-*glucitol*

The estimated standard deviations are given in parentheses and refer to the last decimal position of respective values.

	x	*y*	*z*
C(1)	22562 (85)	3484 (52)	63460 (11)
C(2)	47525 (84)	−4214 (50)	64726 (11)
C(3)	45258 (79)	−9273 (46)	68885 (10)
C(4)	39635 (78)	7370 (53)	71041 (11)
C(5)	14015 (83)	13820 (51)	69704 (10)
C(6)	4366 (91)	29908 (54)	71582 (11)
O(1)	26398 (54)	9477 (30)	59796 (7)
O(2)	53819 (57)	−18743 (37)	62542 (6)
O(3)	68515 (62)	−16905 (37)	70029 (7)
O(4)	37696 (51)	4569 (38)	75012 (8)
O(5)	16054 (52)	17836 (32)	65749 (6)
O(6)	21410 (70)	44119 (35)	71162 (8)
C(1′)	−10397 (95)	49407 (55)	62145 (12)
C(2′)	12822 (88)	46361 (50)	59838 (11)
C(3′)	8636 (88)	34083 (51)	56501 (10)
C(4′)	4174 (80)	15569 (49)	57891 (10)
C(5′)	−3503 (88)	2802 (51)	54791 (11)
C(6′)	17636 (94)	−2616 (59)	52202 (12)
O(1′)	−3203 (58)	60017 (37)	65265 (8)
O(2′)	20219 (63)	62523 (34)	58130 (7)
O(3′)	29915 (70)	34287 (39)	54100 (9)
O(5′)	−14877 (54)	−12118 (33)	56508 (9)
O(6′)	7284 (65)	−13700 (41)	49398 (10)

Table 3. *Fractional atomic coordinates* ($\times 10^4$) *and bond distances* (Å) *of* H *atoms for* 4-*O*-β-D-*glucopyranosyl*-D-*glucitol*

The e.s.d.'s are given in parentheses.

	x	*y*	*z*	C,O–H
H(C1)	970 (68)	−509 (44)	6370 (9)	0·96 (4)
H(C2)	6147 (64)	477 (42)	6464 (9)	1·02 (3)
H(C3)	3141 (63)	−1788 (41)	6920 (9)	1·00 (3)
H(C4)	5311 (64)	1622 (44)	7050 (8)	1·01 (3)
H(C5)	116 (65)	475 (44)	7026 (9)	1·00 (3)
H(C6)	432 (70)	2777 (40)	7443 (9)	1·03 (3)
H′(C6)	−1278 (64)	3443 (45)	7072 (8)	1·02 (3)
H(O2)	6195 (73)	−1492 (49)	6093 (9)	0·78 (4)
H(O3)	6650 (82)	−2461 (41)	7157 (9)	0·82 (3)
H(O4)	5130 (75)	87 (48)	7582 (10)	0·83 (4)
H(O6)	1724 (87)	4909 (51)	6945 (10)	0·75 (4)
H(C1′)	−2430 (67)	5465 (43)	6032 (9)	1·06 (3)
H′(C1′)	−1671 (72)	3877 (43)	6341 (8)	1·00 (3)
H(C2′)	2731 (62)	4166 (45)	6166 (9)	1·07 (3)
H(C3′)	−871 (67)	3725 (51)	5502 (9)	1·09 (4)
H(C4′)	−1184 (67)	1528 (46)	5967 (8)	1·06 (3)
H(C5′)	−1878 (61)	802 (40)	5336 (8)	1·04 (3)
H(C6′)	3054 (74)	−791 (46)	5358 (9)	0·94 (4)
H′(C6′)	2509 (72)	814 (45)	5108 (8)	1·01 (3)
H(O1′)	−1436 (78)	6520 (52)	6600 (11)	0·76 (4)
H(O2′)	2994 (77)	6755 (49)	5955 (10)	0·82 (4)
H(O3′)	3707 (89)	4331 (47)	5408 (11)	0·80 (4)
H(O5′)	−403 (80)	−1842 (50)	5692 (11)	0·77 (4)
H(O6′)	1700 (88)	−1972 (56)	4893 (12)	0·72 (5)

Description of the structure

The conformation of the molecule and the numbering of the atoms are shown in Fig. 1. The glucose and glucitol moieties are denoted by unprimed and primed designators respectively.

Bond distances and angles involving C and O atoms are given in Tables 4 and 5 respectively. The C–C bonds range from 1·496 (7) to 1·539 (6) Å (mean 1·523 Å). The shortening of C(5)–C(6) of the glucose side chain and of the two outer bonds, C(1′)–C(2′) and C(5′)–C(6′), of the glucitol moiety has been observed in many pyranosides (Arnott & Scott, 1972) and in some alditols (Jeffrey & Kim, 1970; Kanters, Roelofsen & Smits, 1977) respectively. The C–O bonds range from 1·397 (5) to 1·449 (5) Å (mean 1·428 Å). The bond lengths in the acetal sequence of bonds C(5)–O(5)–C(1)–O(1)–C(4′) display the characteristic variation observed in α- and β-pyranosides, in that the anomeric C(1)–O(1) is short and that of the ring C–O bonds the bond attached to C(1) is the shorter (Table 4). From observations on crystal structures (Jeffrey & Takagi, 1977; Jeffrey, Pople, Binkley & Vishveshwara, 1978) it is well established that the anomeric C–O is shorter and that the difference between endocyclic C–O bonds is less in β- than in α-pyranosides: for 18 α-pyranosides the mean values of C(1)–O(1), C(5)–O(5) and O(5)–C(1) are

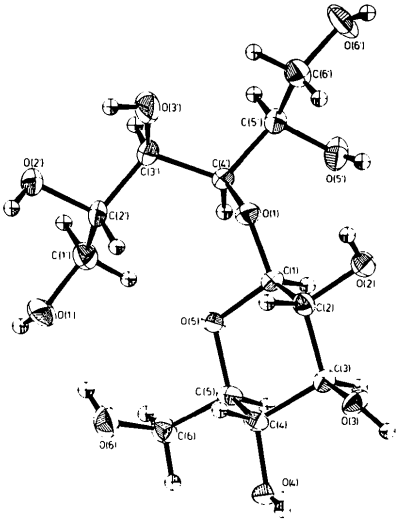

Fig. 1. Molecular conformation and atomic numbering of 4-*O*-β-D-glucopyranosyl-D-glucitol. The glucose and glucitol moieties are denoted by unprimed and primed designators respectively.

1·406, 1·435 and 1·416 Å respectively, for 12 β-pyranosides 1·384, 1·435 and 1·427 Å respectively.

The pertinent values for the title compound (1·397, 1·443 and 1·422 Å) indicate a bond-length variation that is intermediate between that of α- and β-pyranosides. It is noteworthy that the valence angles of the

acetal sequence, C(5)–O(5)–C(1) 113·9° and O(5)–C(1)–O(1) 107·8°, are also intermediate, as follows from the mean values of these angles for α-pyranosides (113·8 and 111·9°) and β-pyranosides (111·5 and 107·7°). In the analogous hexosylpentitol, 4-*O*-β-D-galactopyranosyl-L-rhamnitol (Takagi & Jeffrey, 1977*a*), the acetal geometry is very close to that of the mean for β-pyranosides: C(1)–O(1), C(5)–O(5), O(5)–C(1) 1·384, 1·439, 1·426 Å and C(5)–O(5)–C(1), O(5)–C(1)–O(1) 111·2, 108·6° respectively.

Table 4. *Bond distances* (Å) *for* 4-*O*-β-D-*glucopyranosyl*-D-*glucitol*

The e.s.d.'s are given in parentheses.

C(1)–C(2)	1·519 (6)	C(1′)–C(2′)	1·496 (7)
C(2)–C(3)	1·533 (5)	C(2′)–C(3′)	1·537 (6)
C(3)–C(4)	1·532 (6)	C(3′)–C(4′)	1·539 (6)
C(4)–C(5)	1·522 (6)	C(4′)–C(5′)	1·537 (5)
C(5)–C(6)	1·506 (6)	C(5′)–C(6′)	1·508 (6)
C(1)–O(5)	1·422 (5)	C(1′)–O(1′)	1·433 (5)
C(5)–O(5)	1·443 (4)	C(2′)–O(2′)	1·449 (5)
C(2)–O(2)	1·410 (5)	C(3′)–O(3′)	1·413 (6)
C(3)–O(3)	1·426 (5)	C(4′)–O(1)	1·438 (5)
C(4)–O(4)	1·431 (5)	C(5′)–O(5′)	1·442 (5)
C(6)–O(6)	1·434 (6)	C(6′)–O(6′)	1·426 (6)
C(1)–O(1)	1·397 (5)		

Table 5. *Bond angles* (°) *for* 4-*O*-β-D-*glucopyranosyl*-D-*glucitol*

The e.s.d.'s are given in parentheses.

C(1)–C(2)–C(3)	108·6 (3)	O(1′)–C(1′)–C(2′)	107·2 (4)
C(2)–C(3)–C(4)	106·3 (3)	C(1′)–C(2′)–C(3′)	113·7 (4)
C(3)–C(4)–C(5)	107·2 (3)	C(1′)–C(2′)–O(2′)	108·3 (3)
C(4)–C(5)–O(5)	108·0 (3)	C(3′)–C(2′)–O(2′)	104·7 (3)
C(5)–O(5)–C(1)	113·9 (3)	C(2′)–C(3′)–C(4′)	110·8 (3)
O(5)–C(1)–C(2)	110·5 (3)	C(2′)–C(3′)–O(3′)	110·1 (4)
O(5)–C(1)–O(1)	107·8 (3)	C(4′)–C(3′)–O(3′)	109·0 (3)
C(2)–C(1)–O(1)	106·3 (3)	C(3′)–C(4′)–C(5′)	114·5 (3)
C(1)–C(2)–O(2)	111·0 (3)	C(3′)–C(4′)–O(1)	109·4 (3)
C(3)–C(2)–O(2)	110·1 (3)	C(5′)–C(4′)–O(1)	110·0 (3)
C(2)–C(3)–O(3)	108·3 (3)	C(4′)–C(5′)–C(6′)	114·9 (4)
C(4)–C(3)–O(3)	112·1 (3)	C(4′)–C(5′)–O(5′)	109·1 (3)
C(3)–C(4)–O(4)	112·2 (3)	C(6′)–C(5′)–O(5′)	110·1 (3)
C(5)–C(4)–O(4)	107·1 (3)	C(5′)–C(6′)–O(6′)	108·0 (4)
C(4)–C(5)–C(6)	115·9 (3)		
O(5)–C(5)–C(6)	106·1 (3)		
C(5)–C(6)–O(6)	112·3 (4)	C(1)–O(1)–C(4′)	115·4 (3)

The C–C–C angles range from 106·3 (3) to 115·9 (3)° (mean 111·5°), the C–C–O angles from 104·7 (3) to 112·3 (4)° (mean 109·0°). The exocyclic angles at C(5) show the familiar trend of pyranosides that C(4)–C(5)–C(6) (115·9°) is enlarged at the expense of O(5)–C(5)–C(6) (106·1°) (Arnott & Scott, 1972). The bridge angle C(1)–O(1)–C(4′) is 115·4° and agrees with bridge angles of (1→4)-linked glycosides.

The C–H and O–H bond lengths, which are included in Table 3, average 1·02 and 0·78 Å respectively. The bond angles involving H atoms have mean values distributed over the different classes as follows: H–C–C 109, H–C–O 110, H–O–C 109 and H–C–H 109°.

The ring torsion angles (Table 6) vary from 57·3 (4) to 64·3 (4)° (mean 60·9°). Though these values are within the range commonly observed, the mean value is larger than that reported for pyranose rings in mono- and disaccharides, which are about 58° (Hirotsu & Shimada, 1974; Jeffrey, McMullan & Takagi, 1977). This is mainly due to the torsion angles about C(2)–C(3) and C(3)–C(4) (mean 62·2°), which deviate nearly 8° from the mean value observed in saccharide structures. Accordingly, the ring-puckering parameters of Cremer & Pople (1975) (q_2 = 0·082 Å, q_3 = 0·623 Å, Q = 0·628 Å, θ = 7·5° and φ = 213°) and the average deviation of atoms from the three least-squares planes through opposite bonds [0·023 Å from plane C(1), C(2), C(4), C(5), 0·033 Å from C(3), C(4), O(5), C(1) and 0·011 Å from C(2), C(3), C(5), O(5)] indicate a distorted $^4C_1$ chair.

The exocyclic torsion angles (Table 6) have values close to 60 or 180° which correspond to the ideal *gauche* or *trans* arrangements respectively. The confor-

Table 6. *Endo- and exocyclic torsion angles* (°) *for the glucopyranosyl moiety of* 4-*O*-β-D-*glucopyranosyl*-D-*glucitol*

The torsion angle $A(1)$–$A(2)$–$A(3)$–$A(4)$ is viewed along $A(2)$–$A(3)$, with a clockwise rotation of $A(1)$ to $A(4)$ taken to be positive.

Endocyclic					
O(5)–C(1)–C(2)–C(3)	57·3 (4)	C(2)–C(3)–C(4)–C(5)	64·3 (4)	C(4)–C(5)–O(5)–C(1)	61·1 (4)
C(1)–C(2)–C(3)–C(4)	−60·9 (4)	C(3)–C(4)–C(5)–O(5)	−63·2 (4)	C(5)–O(5)–C(1)–C(2)	−58·3 (4)
Exocyclic					
O(5)–C(1)–C(2)–O(2)	178·4 (3)	O(3)–C(3)–C(4)–C(5)	−177·6 (3)	O(5)–C(5)–C(6)–O(6)	−61·8 (4)
O(1)–C(1)–C(2)–C(3)	174·0 (3)	O(3)–C(3)–C(4)–O(4)	−60·3 (4)	C(5)–O(5)–C(1)–O(1)	−174·1 (3)
O(1)–C(1)–C(2)–O(2)	−64·9 (4)	C(3)–C(4)–C(5)–C(6)	178·0 (3)	C(6)–C(5)–O(5)–C(1)	−174·0 (3)
C(1)–C(2)–C(3)–O(3)	178·5 (3)	O(4)–C(4)–C(5)–O(5)	176·2 (3)		
O(2)–C(2)–C(3)–C(4)	177·4 (3)	O(4)–C(4)–C(5)–C(6)	57·4 (4)	O(5)–C(1)–O(1)–C(4′)	−68·2 (4)
O(2)–C(2)–C(3)–O(3)	56·8 (4)	C(4)–C(5)–C(6)–O(6)	58·0 (5)	C(2)–C(1)–O(1)–C(4′)	173·3 (3)
C(2)–C(3)–C(4)–O(4)	−178·4 (3)				

mation about exocyclic C(5)–C(6) is *gauche–gauche*, identical to that of β-D-glucose (Chu & Jeffrey, 1968).

The glucitol residue has a non-planar carbon-chain conformation which is derived from the planar extended chain by a rotation of 120° about C(2′)–C(3′) and C(4′)–C(5′) (Table 7).

As Jeffrey & Kim (1970) have pointed out, alditols adopt a conformation with a planar extended carbon chain, provided this does not imply conformational states with parallel C–(*n*)–O/C–(*n* + 2)–O bonds. In that case the carbon chain adopts a bent non-planar conformation. Observations on a number of crystalline alditols (Jeffrey & Kim, 1970), including D-glucitol, are consistent with this hypothesis. However, the conformation of the glucitol residue of D-glucosyl-D-glucitol is *MAA** which differs from that found in the *A* form of D-glucitol (Park, Jeffrey & Hamilton, 1971) and in the D-glucitol–pyridine complex (Kim, Jeffrey & Rosenstein, 1971), which both have the stable *MAP* bent-chain conformation (Fig. 2) predicted by the above hypothesis. The observed *MAA* conformation is unstable because of the almost parallel orientation of the C(5′)–C(6′) and C(3′)–O(3′) bonds (angle 8·6°). The terminal hydroxyl groups of the glucitol residue and the *A* form of D-glucitol have the same extended *AA* conformation, whereas in D-glucitol–pyridine these conformations are both bent (see Table 7 and Fig. 2). Clearly, environmental effects in the crystal not only determine the conformation of the terminal hydroxyl groups, but also strongly influence the carbon-chain conformation, which so far on stereochemical considerations and experimental results has been considered as a predominantly molecular property (Jeffrey & Kim, 1970).

The torsion angles involving H atoms on adjacent C atoms (Table 8) differ little from the ideal *trans* or *gauche* arrangements (mean deviation 4°), whereas with one exception [H(C4)···H(O4) −61 (3)°] the H–C–O–H torsion angles show large deviations (mean 38°) from the ideal value of 60° which would be favoured by the isolated molecule (Sundaralingam, 1968; Takagi & Jeffrey, 1977*b*). This behaviour, which is widespread in carbohydrate structures, is caused by intermolecular hydrogen bonding which offsets the loss in energy resulting from the eclipsing of vicinal H atoms.

The torsion angles characterizing the glycosidic linkage are φ_1[O(5)–C(1)–O(1)–C(4′)] = −68·2 (4)°

Table 7. *Torsion angles* (°) *for the glucitol moiety of* 4-*O*-β-D-*glucopyranosyl*-D-*glucitol with corresponding values for* D-*glucitol and the glucitol moiety of the glucitol–pyridine complex*

	4-*O*-β-D-Glucopyranosyl-D-glucitol[a]	D-Glucitol[b]	Glucitol–pyridine[c]
O(1′)–C(1′)–C(2′)–C(3′)	176·1 (3)	−173·9 (3)	−58·7 (3)
O(1′)–C(1′)–C(2′)–O(2′)	−68·0 (4)	−55·4 (3)	62·6 (3)
C(1′)–C(2′)–C(3′)–C(4′)	−69·7 (4)	−52·4 (3)	−69·5 (3)
C(1′)–C(2′)–C(3′)–O(3′)	169·5 (3)	−174·3 (3)	169·6 (2)
O(2′)–C(2′)–C(3′)–C(4′)	172·2 (3)	−173·4 (2)	171·2 (2)
O(2′)–C(2′)–C(3′)–O(3′)	51·5 (4)	64·8 (3)	50·4 (3)
C(2′)–C(3′)–C(4′)–C(5′)	172·7 (3)	−178·1 (2)	161·3 (2)
C(2′)–C(3′)–C(4′)–O(1)	−63·4 (4)	−54·5 (3)	−75·4 (3)
O(3′)–C(3′)–C(4′)–C(5′)	−66·0 (4)	−56·5 (3)	−78·2 (3)
O(3′)–C(3′)–C(4′)–O(1)	57·9 (4)	67·1 (3)	45·1 (3)
C(3′)–C(4′)–C(5′)–C(6′)	74·4 (4)	−179·8 (2)	178·6 (2)
C(3′)–C(4′)–C(5′)–O(5′)	−161·6 (3)	−55·4 (3)	−57·6 (3)
O(1)–C(4′)–C(5′)–C(6′)	−49·3 (4)	57·2 (3)	55·0 (3)
O(1)–C(4′)–C(5′)–O(5′)	74·8 (4)	−178·4 (3)	178·7 (2)
C(4′)–C(5′)–C(6′)–O(6′)	−177·2 (3)	−174·1 (3)	70·6 (3)
O(5′)–C(5′)–C(6′)–O(6′)	59·2 (4)	62·3 (4)	−52·4 (3)
C(3′)–C(4′)–O(1)–C(1)	125·1 (3)		
C(5′)–C(4′)–O(1)–C(1)	−108·4 (4)		

References: (*a*) this article, (*b*) Park, Jeffrey & Hamilton (1971), (*c*) Kim, Jeffrey & Rosenstein (1971).

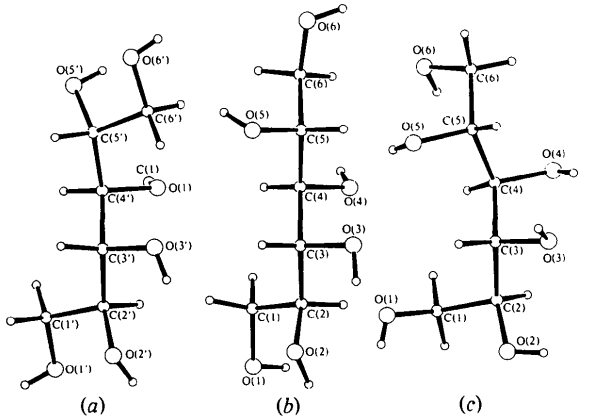

Fig. 2. Views of the glucitol moieties of (*a*) 4-*O*-β-D-glucopyranosyl-D-glucitol, (*b*) D-glucitol (Park, Jeffrey & Hamilton, 1971) and (*c*) the D-glucitol–pyridine complex (Kim, Jeffrey & Rosenstein, 1971) along the bisector of C(2′)–C(3′)–C(4′).

* *M*, *A* and *P* refer to the conformation about C–C bonds; *M* = *Msc*, *A* = *ap* and *P* = *Psc*, according to the convention of Klyne & Prelog (1960).

Table 8. *Torsion angles* (°) *involving the hydrogen atoms for* 4-*O*-β-D-*glucopyranosyl*-D-*glucitol*

H(C1)···H(C2)*	−177 (3)	H(C2)···H(O2)†	−32 (3)
H(C2)···H(C3)	178 (3)	H(C3)···H(O3)	−26 (3)
H(C3)···H(C4)	−175 (3)	H(C4)···H(O4)	−61 (3)
H(C4)···H(C5)	180 (3)	H(C6)···H(O6)	−151 (3)
H(C5)···H(C6)	65 (3)	H′(C6)···H(O6)	−35 (4)
H(C5)···H′(C6)	−60 (3)		
H(C1′)···H(C2′)	177 (3)	H(C1′)···H(O1′)	35 (4)
H′(C1′)···H(C2′)	−60 (3)	H′(C1′)···H(O1′)	−87 (4)
H(C2′)···H(C3′)	167 (3)	H(C2′)···H(O2′)	−29 (3)
H(C3′)···H(C4′)	−60 (3)	H(C3′)···H(O3′)	93 (4)
H(C4′)···H(C5′)	66 (3)	H(C5′)···H(O5′)	158 (4)
H(C5′)···H(C6′)	−176 (3)	H(C6′)···H(O6′)	−26 (4)
H(C5′)···H′(C6′)	68 (3)	H′(C6′)···H(O6′)	94 (4)

* Refers to the torsion angle H(C1)–C(1)–C(2)–H(C2).
† Refers to the torsion angle H(C2)–C(2)–O(2)–H(O2).

Table 9. *Geometry of the hydrogen bonds in* 4-*O*-β-D-*glucopyranosyl*-D-*glucitol*

Number		O–H (Å)	H···O (Å)	H···O* (Å)	O···O (Å)	O–H···O (°)	O–H···O* (°)	Symmetry operation†
1	O(2)–H(O2)···O(5′)	0·77 (4)	2·01 (4)	1·83	2·758 (4)	164 (4)	162	655.1
2	O(3)–H(O3)···O(4)	0·82 (3)	2·04 (3)	1·89	2·850 (4)	174 (3)	174	646.4
3	O(4)–H(O4)···O(6)	0·83 (4)	1·87 (4)	1·75	2·682 (4)	165 (4)	164	646.4
4	O(6)–H(O6)···O(1′)	0·75 (4)	2·02 (4)	1·83	2·759 (4)	165 (5)	163	555.1
5	O(1′)–H(O1′)···O(2)	0·76 (4)	2·43 (4)	2·31	2·973 (4)	129 (4)	126	465.1
6	O(1′)–H(O1′)···O(3)	0·76 (4)	2·19 (4)	2·02	2·885 (4)	152 (4)	149	465.1
7	O(2′)–H(O2′)···O(2)	0·82 (4)	1·96 (4)	1·83	2·782 (4)	174 (4)	174	565.1
8	O(3′)–H(O3′)···O(6′)	0·80 (4)	2·28 (4)	2·14	2·978 (5)	147 (4)	145	556.3
9	O(3′)–H(O3′)···O(2′)	0·80 (4)	2·26 (4)	2·20	2·669 (4)	113 (4)	109	555.1
10	O(5′)–H(O5′)···O(2′)	0·77 (4)	2·01 (4)	1·82	2·769 (4)	171 (4)	171	545.1
11	O(6′)–H(O6′)···O(5′)	0·72 (4)	2·58 (4)	2·38	3·179 (4)	143 (4)	140	546.3
12	O(6′)–H(O6′)···O(6′)	0·72 (5)	2·56 (5)	2·35	3·206 (4)	151 (4)	148	546.3

* 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 acceptor O atoms. The first set of numbers specifies the lattice translations, *e.g.* 645.4 is $+a - b$ from 555.4. The last digit indicates one of the following symmetry operations: (1) x,y,z; (2) $\frac{1}{2} - x, -y, \frac{1}{2} + z$; (3) $\frac{1}{2} + x, \frac{1}{2} - y, -z$; (4) $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

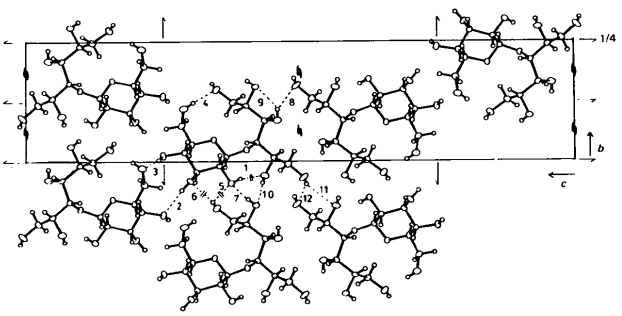

Fig. 3. A view of the molecular packing and hydrogen bonds of 4-*O*-β-D-glucopyranosyl-D-glucitol seen along **a**. Hydrogen bonds, numbered according to Table 9, are indicated by dashed lines.

and φ_2[C(1)–O(1)–C(4′)–C(3′)] = 125·1 (3)°. The torsion angle φ_1 is close to −71°, which is the preferred conformation for methyl β-pyranosides (Takagi & Jeffrey, 1977*a*), whereas the arrangement of bonds about O(1)–C(4′) is nearly eclipsed. In D-galactosyl-L-rhamnitol the corresponding angles are −70·8° and −127·8° respectively. In a recent study Pérez & Marchessault (1978) have pointed out that for oligosaccharides the range of φ_1 is much more restricted than that of φ_2 and they interpreted the relative invariance of φ_1 as a manifestation of the *exo* anomeric effect. As the presence of an intramolecular hydrogen bond, which connects contiguous residues, is a common feature of β-(1→4)-linked disaccharides (Sundaralingam, 1968; Hirotsu & Shimada, 1974), the restricted rotation about anomeric C(1)–O(1) would imply that in the formation of intramolecular hydrogen bonds the rotational flexibility about O(1)–C(4′) plays the dominant role.

The hydrogen bonding

The hydrogen-bond geometry is described in Table 9 and illustrated in Fig. 3. The nine hydroxyl groups all act as hydrogen-bond donors to form twelve hydrogen bonds. Three hydroxyl groups, O(1′)–H, O(3′)–H and O(6′)–H, are involved in interactions of the bifurcated type, O(3)–H is not an acceptor and O(5′)–H and O(6′)–H are double acceptors, whereas ring O(5) and glycosidic O(1) do not accept a hydrogen bond. The presence of two intramolecular hydrogen bonds, one of which is involved in a bifurcated bond, and three bifurcated interactions give rise to an unusual and complicated hydrogen-bond pattern. There are three infinite donor–acceptor chains: O(6)→O(1′)→O(3)→O(4)→O′(6), O(2′)→O(2)→O(5′)→O′(2′) and O(6′)→O′(6′), which are mutually connected by bifurcated hydroxyl groups. With the exception of the bifurcated bonds, the H···O distances span the narrow range 1·75 to 1·89 Å.

The intramolecular hydrogen bond O(6)–H···O(1′), with H···O 1·83 Å and O–H···O 163°, is a strong interaction stabilizing the conformation of the glycosidic linkage, whereas the other intramolecular bond, O(3′)–H···O(2′), which is a branch of a bifurcated interaction, with O–H···O 109° should be considered as a weak interaction. Of the three bifurcated bonds two are of the symmetrical type and one is asymmetrical. Although bifurcated interactions have been reported for methyl α-D-altropyranoside (Poppleton, Jeffrey & Williams, 1975), α-L-sorbose (Kim & Rosenstein, 1967) and β-D-fructose (Takagi & Jeffrey, 1977*c*), their occurrence in saccharide structures is rare and the presence of three such bonds in a single structure represents a unique case. A remarkable feature of these bifurcated bonds is the near coplanarity of the H atom with the three

surrounding O atoms. For the three bonds involving O(1′)—H, O(3′)—H and O(6′)—H the distances of the H atoms from the plane of the O atoms are 0·13, 0·16 and 0·02 Å respectively.

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The Crystal and Molecular Structure of 7-(Methyl 2-acetamido-6-*O*-acetyl-2,3,4-trideoxy-α-D-*threo*-hex-2-enopyranosid-4-yl)theophylline, $C_{18}H_{23}N_5O_7$

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Abstract

The title compound, $C_{18}H_{23}N_5O_7$, crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 13·1444 (4), b = 14·9593 (4), c = 10·5007 (3) Å, Z = 4. The structure was refined to an R of 0·037. The orientation of the base relative to the sugar ring, defined in terms of rotation about the C(4′)—N(7) glycosyl bond, is *anti* (−81·0°). The base conformation can be described by the mean values of the torsion angles of 1·8 and 0·0° for the six- and five-membered rings respectively. The sugar moiety exhibits a half-chair $^0H_5$

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