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Structure of Lactitol (4-*O*-β-D-Galactopyranosyl-D-glucitol) Monohydrate: an Artificial Sweetner

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Abstract. $C_{12}H_{24}O_{11}.H_2O$, $M_r = 362{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}808$ (2), $b = 12{\cdot}685$ (2), $c = 15{\cdot}931$ (3) Å, $V = 1577{\cdot}9$ (6) Å^3, $Z = 4$, $D_x = 1{\cdot}525$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}13$ mm^{-1}, $F(000) = 776$, $T = 295$ K, $R = 0{\cdot}031$ for 1781 unique reflections with $I > 2{\cdot}5\sigma(I)$. The galactopyranosyl ring has the $^4C_1$ chair conformation and the conformation of the bent glucitol C-atom chain is *MAA*. The torsion angles characterizing the conformation of the glycosidic linkage are −86·3 (2)° [O(5)—C(1)—O(1)—C(14)] and 116·8 (2)° [C(1)—O(1)—C(14)—C(13)]. All hydroxyl groups act as donors in hydrogen bonds; three bonds are intramolecular. With the exception of O(1) of the glycosidic link which is not an acceptor and O(6) of the glucitol residue which is a double acceptor, all O atoms accept one hydrogen bond. The water molecule donates two and accepts one hydrogen bond.

Introduction. Information on the conformation of carbohydrate derivatives consisting of cyclic pyranosides and acyclic polyalcohols is very limited. So far the structures of five members of this class have been reported. Takagi & Jeffrey (1977) reported the structure of 4-*O*-β-D-galactopyranosyl-L-rhamnitol (GR), Gaykema & Kanters (1979) that of 4-*O*-β-D-glucopyranosyl-D-glucitol (cellobiotol, GG1), Lindner & Lichtenthaler (1981) that of 1-*O*-α-D-glucopyranosyl-D-mannitol (GM), Lichtenthaler & Lindner (1981) that of 6-*O*-α-D-glucopyranosyl-D-glucitol (isomaltitol, GG2) and Ohno, Hirao & Kido (1982) that of 4-*O*-α-D-glucopyranosyl-D-glucitol (maltitol, GG3). The growing interest in this type of compound is directed towards a better understanding of the influence of the pyranoside moiety on the conformation of the alditol chain and more recently at tracing the relationship between conformation and sweetening properties. The title compound, which is entirely nontoxic, is considered as a potential artificial sweetner and food additive (van Velthuijsen, 1979) with a sweetness of about 35% of that of sucrose (Saijonmaa, Heikonen, Kreula & Linko, 1978), whereas the nutritional value is much smaller than would be expected from its theoretical energy content (Hayashibara & Sugimoto, 1976). For this reason lactitol offers many promising applications for the food industry, in particular in the fields of dietetic and low-calorie foods.

In the β-linked pyranosylalditols GR and GG1, the torsion angles O(5)—C(1)—O(1)—C(14) about the anomeric C—O bond are −70·8 (2) and −68·2 (4)° respectively, which is close to the preferred conformation for methyl-β-pyranosides (−71°) (Takagi & Jeffrey, 1977), whereas the torsion angles about the other C—O bond of the link amount to −127·8 (2) and 125·1 (3)° respectively. In α-(1→4)-linked GM, GG2 and GG3, the torsion angles about the anomeric C—O bond are 74·6 (8), 77·9 (8) and 73·0 (3)° respectively. In order to elucidate the conformation about the anomeric C—O bond of β-(1→4)-linked pyranosylalditols we undertook the structure analysis of lactitol monohydrate.

Experimental. Rod-shaped crystals of the monohydrate were obtained by slow evaporation of a 50% ethanol–water solution at room temperature. The melting point of the single crystals measured on a Leitz Heiztisch microscope is 393–394 K. A crystal of dimensions 0·2 × 0·4 × 0·5 mm was used for data collection. Cell dimensions were derived from the setting angles of 24 reflections with $15{\cdot}2 \le \theta \le 19{\cdot}6°$. Data were collected on an Enraf–Nonius CAD-4 diffractometer (Zr-filtered Mo $K\alpha$ radiation, θ–2θ scan). 2081 reflections were measured (h 0 ≤ 10, k 0 ≤ 16, l 0 ≤ 20, $\theta_{max} = 27{\cdot}5°$) of which 1781 with $I > 2{\cdot}5\sigma(I)$ were considered observed. Two standard reflections (112 and 1$\bar{1}$2) measured every hour

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showed insignificant variations. Intensities were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined on F by least-squares techniques with the *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) package. All H atoms were located in difference maps and included in the refinement with constant isotropic thermal parameters equal to those of the carrier atoms. Full-matrix least-squares refinement of 295 parameters including scale factor, coordinates and anisotropic thermal parameters of non-H atoms and coordinates of the H atoms converged at $R = 0{\cdot}031$, $wR = 0{\cdot}035$ with $w = 1/[\sigma^2(F_o) + 0{\cdot}003F_o^2]$, $S = 1{\cdot}14$, $(\Delta/\sigma)_{max} = 0{\cdot}63$. Minimum and maximum residual electron densities in the final difference Fourier map are $-0{\cdot}25$ and $0{\cdot}31$ e Å^{-3} respectively. Calculations were carried out on an in-house MicroVAX II and on the Cyber 180–855 of the Utrecht University Computer Center. The program package *EUCLID* (Spek, 1982) was used for the calculation of geometries and preparation of illustrations. Scattering factors for H atoms were taken from Stewart, Davidson & Simpson (1965) and for C and O atoms from Cromer & Mann (1968).

Discussion. The final atomic coordinates and equivalent isotropic thermal parameters of the non-H atoms are listed in Table 1.* The conformation and atomic numbering of the title compound are shown in Fig. 1. Bond distances, angles and selected torsion angles are listed in Table 2. The C—C bond lengths are in the range 1·504 (3)–1·538 (3) Å and three C—C bonds of the primary alcohol groups show significant shortening. This shortening has also been observed in GG1 and GG3, and in many pyranosides (Arnott & Scott, 1972) as well as in some alditols (Kanters, Roelofsen & Smits, 1977). The C—O bonds are in the range 1·394 (3)–1·452 (3) Å (mean 1·426 Å). The anomeric C(1)—O(1) bond is shortened [1·394 (3) Å] as is often observed in α- and β-pyranosides (Arnott & Scott, 1972). However, the often observed discrepancy of the endocyclic bond lengths is absent, which is in accordance with the reported minor differences of these lengths in β-pyranoses (Jeffrey & Takagi, 1977; Jeffrey, Pople, Binkley & Vishveshwara, 1978).

The angles in the acetal sequence, C(5)—O(5)—C(1) 111·4 (2) and O(5)—C(1)—O(1) 108·1 (2)°, compare well with the average values of 111·5 and 107·4° respectively found in 12β-pyranosides (Jeffrey *et al.*, 1978). The C—C—C angles are in the range 108·9 (2)–116·4 (2)° (average 111·9°); the C—C—O angles vary from 104·8 (2) to 115·2 (2)° (average 109·2°). The glycosidic angle C(1)—O(1)—C(14) [118·2 (2)°] is larger than the corresponding angles in GG1 [115·4 (3)°] and GR [115·8 (1)°] and also outside the range of 115·8–117·1° reported for six β-(1→4)-linked disaccharides (Hirotsu & Shimada, 1974).

The endocyclic torsion angles are in the range 49·9 (2)–65·7 (2)° which agrees well with the range of 52·4 (1)–65·3 (1)° observed in β-D-galactose (Longchambon, Ohanessian, Avenel & Neuman,

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
O(1)	0·1828 (2)	0·2727 (1)	0·33893 (9)	0·0187 (8)
O(2)	0·0251 (2)	0·4672 (1)	0·3810 (1)	0·0274 (8)
O(3)	0·1549 (2)	0·5545 (1)	0·5341 (1)	0·0287 (9)
O(4)	0·3886 (2)	0·3968 (1)	0·57729 (9)	0·0262 (9)
O(5)	0·4246 (2)	0·3222 (1)	0·40908 (9)	0·0217 (8)
O(6)	0·7824 (2)	0·3132 (1)	0·4052 (1)	0·0293 (9)
O(11)	0·6239 (2)	0·2543 (1)	0·2514 (1)	0·0325 (9)
O(12)	0·4913 (2)	−0·0107 (1)	0·3165 (1)	0·0338 (9)
O(13)	0·1651 (2)	0·0616 (1)	0·3219 (1)	0·0304 (9)
O(15)	0·0885 (2)	0·1736 (1)	0·12805 (9)	0·0308 (9)
O(16)	−0·1485 (2)	0·3468 (1)	0·1420 (1)	0·0275 (9)
O(111)	0·3609 (3)	0·2349 (1)	0·0237 (1)	0·053 (1)
C(1)	0·2765 (3)	0·3598 (2)	0·3663 (1)	0·0190 (9)
C(2)	0·1629 (3)	0·4212 (2)	0·4269 (1)	0·020 (1)
C(3)	0·2611 (3)	0·5088 (2)	0·4715 (1)	0·0212 (9)
C(4)	0·4271 (3)	0·4665 (2)	0·5088 (1)	0·021 (1)
C(5)	0·5255 (3)	0·4072 (2)	0·4408 (1)	0·021 (1)
C(6)	0·6904 (3)	0·3613 (2)	0·4731 (1)	0·025 (1)
C(11)	0·6086 (3)	0·1428 (2)	0·2535 (2)	0·032 (1)
C(12)	0·4676 (3)	0·1008 (2)	0·3093 (1)	0·023 (1)
C(13)	0·2893 (3)	0·1136 (2)	0·2718 (1)	0·0196 (9)
C(14)	0·2273 (3)	0·2262 (2)	0·2586 (1)	0·0180 (9)
C(15)	0·0627 (3)	0·2279 (2)	0·2056 (1)	0·0206 (9)
C(16)	0·0127 (3)	0·3402 (2)	0·1843 (1)	0·024 (1)

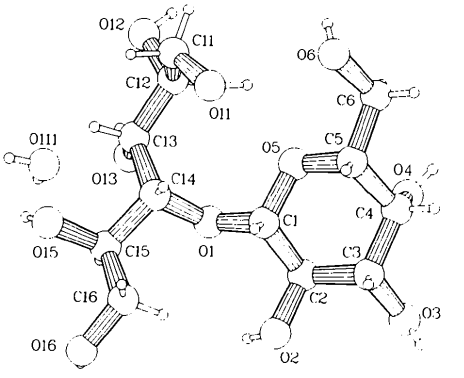


Fig. 1. Perspective view of the conformation with atom numbering.

* Lists of structure factors, anisotropic thermal parameters of non-H atoms, coordinates of H atoms and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53138 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

O(1)—C(1)	1·394 (3)	O(16)—C(16)	1·430 (3)
O(1)—C(14)	1·452 (3)	C(1)—C(2)	1·525 (3)
O(2)—C(2)	1·425 (3)	C(2)—C(3)	1·525 (3)
O(3)—C(3)	1·421 (3)	C(3)—C(4)	1·524 (3)
O(4)—C(4)	1·436 (3)	C(4)—C(5)	1·527 (3)
O(5)—C(1)	1·425 (3)	C(5)—C(6)	1·504 (3)
O(5)—C(5)	1·427 (3)	C(11)—C(12)	1·513 (3)
O(6)—C(6)	1·434 (3)	C(12)—C(13)	1·523 (3)
O(11)—C(11)	1·419 (3)	C(13)—C(14)	1·523 (3)
O(12)—C(12)	1·431 (3)	C(14)—C(15)	1·538 (3)
O(13)—C(13)	1·419 (3)	C(15)—C(16)	1·517 (3)
O(15)—C(15)	1·429 (3)		

C(1)—O(5)—C(5)	111·4 (2)	C(4)—C(5)—C(6)	112·2 (2)
C(1)—O(1)—C(14)	118·2 (2)	O(6)—C(6)—C(5)	109·6 (2)
O(1)—C(1)—O(5)	108·1 (2)	O(11)—C(11)—C(12)	115·2 (2)
O(1)—C(1)—C(2)	107·3 (2)	O(12)—C(12)—C(11)	107·5 (2)
O(5)—C(1)—C(2)	109·9 (2)	O(12)—C(12)—C(13)	104·8 (2)
O(2)—C(2)—C(1)	108·9 (2)	C(11)—C(12)—C(13)	113·4 (2)
O(2)—C(2)—C(3)	108·7 (2)	O(13)—C(13)—C(12)	110·8 (2)
C(1)—C(2)—C(3)	112·0 (2)	O(13)—C(13)—C(14)	107·3 (2)
O(3)—C(3)—C(2)	109·3 (2)	C(12)—C(13)—C(14)	116·4 (2)
O(3)—C(3)—C(4)	111·4 (2)	O(1)—C(14)—C(13)	109·6 (2)
C(2)—C(3)—C(4)	110·7 (2)	O(1)—C(14)—C(15)	106·2 (2)
O(4)—C(4)—C(3)	109·6 (2)	C(13)—C(14)—C(15)	110·8 (2)
O(4)—C(4)—C(5)	110·0 (2)	O(15)—C(15)—C(14)	110·5 (2)
C(3)—C(4)—C(5)	108·9 (2)	O(15)—C(15)—C(16)	107·2 (2)
O(5)—C(5)—C(4)	110·2 (2)	C(14)—C(15)—C(16)	110·6 (2)
O(5)—C(5)—C(6)	107·5 (2)	O(16)—C(16)—C(15)	112·8 (2)

C(14)—O(1)—C(1)—O(5)	−86·3 (2)	O(11)—C(11)—C(12)—O(12)	−169·1 (2)
C(1)—O(1)—C(14)—C(13)	116·8 (2)	O(12)—C(12)—C(13)—O(13)	55·9 (2)
C(11)—C(12)—C(13)—C(14)	−64·3 (2)	O(13)—C(13)—C(14)—O(1)	50·7 (2)
C(12)—C(13)—C(14)—C(15)	169·2 (2)	O(1)—C(14)—C(15)—O(15)	−174·0 (2)
C(13)—C(14)—C(15)—C(16)	−173·6 (2)	O(15)—C(15)—C(16)—O(16)	65·2 (2)

Table 3. *Geometry of hydrogen bonds*

	O—H (Å)	H···O (Å)	O···O (Å)	O—H···O (°)	Symmetry operation*
O(2)—H···O(6)	0·83 (2)	1·96 (2)	2·749 (2)	158 (2)	455.1
O(3)—H···O(111)	0·81 (2)	1·87 (2)	2·679 (2)	173 (2)	565.4
O(4)—H···O(13)	0·78 (2)	2·00 (2)	2·741 (2)	161 (2)	556.2
O(6)—H···O(4)	0·79 (2)	2·03 (2)	2·803 (2)	165 (2)	556.2
O(11)—H···O(5)	0·86 (2)	2·50 (2)	3·078 (2)	125 (2)	555.1
O(11)—H···O(6)	0·86 (2)	2·02 (2)	2·846 (2)	159 (2)	555.1
O(12)—H···O(3)	0·85 (2)	1·91 (2)	2·758 (2)	179 (3)	556.2
O(13)—H···O(16)	0·74 (2)	2·11 (2)	2·787 (2)	152 (2)	545.3
O(13)—H···O(12)	0·74 (2)	2·34 (2)	2·708 (2)	112 (2)	555.1
O(15)—H···O(2)	0·85 (2)	1·95 (2)	2·768 (2)	163 (2)	545.3
O(16)—H···O(11)	0·83 (2)	1·93 (2)	2·752 (2)	173 (2)	455.1
O(111)—H···O(16)	0·81 (3)	2·02 (3)	2·837 (2)	178 (3)	555.2
O(111)—H′···O(15)	0·87 (3)	1·96 (3)	2·810 (2)	164 (2)	555.1

* The symmetry operation is performed on the acceptor O atom. The first set of numbers specifies the lattice translations, *e.g.* 456.4 is $-a+c$ from 555.4. 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) $\frac{1}{2}-x, -y, \frac{1}{2}+z$. The symmetry operation 555.1 is assigned to the donor OH groups.

1975). The Cremer & Pople (1975) puckering parameters θ and φ are 6·6 (2) and 327·0 (2)° respectively, which indicates a weakly distorted $^4C_1$ chair conformation. The exocyclic torsion angles are close to the ideal values of 60 or 180°, the mean deviation amounts to 5·2°. The conformation of the exocyclic C(6)—O(6) bond is *gauche–trans* as in β-D-galactose and the majority of galactosylpyranosides (Longchambon *et al.*, 1975).

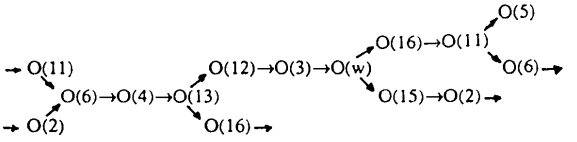
The glucitol fragment has a non-planar, bent *MAA** C-chain conformation which can be derived from the planar chain by a 120° rotation about C(12)—C(13), thus avoiding the unfavourable conformation with parallel C(12)—O(12)/C(14)—O(1) bonds (Jeffrey & Kim, 1970). This *MAA* conformation was also found in the *A* form of D-glucitol (Park, Jeffrey & Hamilton, 1971), in the D-glucitol–pyridine complex (Kim, Jeffrey & Rosenstein, 1971) and in isomaltitol (GG2) (Lichtenthaler & Lindner, 1981), whereas cellobiotol (GG1) (Gaykema & Kanters, 1979) has the unfavourable *MAP** conformation with almost parallel C(13)—O(13)/C(15)—C(16) bonds. Interestingly, the orientation of the terminal C—O bonds with respect to the adjacent C—C bonds of the two glucitols and the three pyranosylglucitols is variable. In GG1, GG2 and D-glucitol the orientations are both extended, in GG3 extended and bent respectively, in the D-glucitol–pyridine complex both bent, and in the title compound bent and extended respectively. As has already been pointed out by Jeffrey & Kim (1970), it is reasonable to assume that these differences are a result of intermolecular forces in the crystal. However, intramolecular interactions may also be operative, as is exemplified by the formation in the title compound and also in GG1 of an intramolecular hydrogen bond [O(11)—H···O(6) and O(6)—H···O(11) respectively] made possible by the bent and extended orientations respectively of the C(11)—O(11) bond.

The torsional angles characterizing the glycosidic link φ_1 [O(5)—C(1)—O(1)—C(14)] and φ_2 [C(1)—O(1)—C(14)—C(13)] are −86·3 (2) and 116·8 (2)° respectively. The angle φ_1 is very close to the average value of −84·9° observed in 14 disaccharides having β-(1→x) glycosidic linkages (Ohanessian, Avenel, Neuman & Gillier-Pandraud, 1980). For the pyranosylalditols GG1 and GR the φ_1 angles are −68·2 (4) and −70·8 (2)° respectively. As in β-(1→4)-linked disaccharides and the pyranosylalditols GG1 and GR, φ_2 in the title compound [116·8 (2)°] approaches the value corresponding to an eclipsed conformation about O(1)—C(14).

All 11 potential hydrogen-bond donors are involved in a three-dimensional system of 13 hydrogen bonds (Table 3). With the exception of glycosidic O(1) which is not an acceptor and O(6) which is a double acceptor, all O atoms act as a single acceptor. Two donors O(11)—H and O(13)—H participate in asymmetric bifurcated hydrogen bonds, the former donor being connected to two intramolecular acceptors. These four-atom hydrogen-bond configurations are planar as follows from the sum of angles

* *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).

around the central H atom, which amount to 360 (3) and 359 (3)° respectively. The water molecule donates two hydrogen bonds and accepts one, thus serving as an important cohesive element in the hydrogen-bond system. This system consists of a finite chain which stops at ring O(5) and an infinite one which branches at the bifurcated donors and also at the water molecule. This system can be schematically represented (see below).



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Functionalized Hydrocarbons with Condensed Ring Skeletons. X. A Methyltricyclo[7.4.0.0^{2,6}]tetradec-7-ene

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Abstract. (1) 1,9-*trans*-1,2-*cisoid*-2,6-*cis*-4,11,11-Tris(methoxycarbonyl)-6-methyltricyclo[7.4.0.0^{2,6}]-tridec-7-ene-4,2-carbolactone, $C_{21}H_{26}O_8$, M_r = 406·43, monoclinic, $P\bar{1}$, a = 6·0774 (2), b = 12·3784 (5), c = 14·2565 (4) Å, α = 72·906 (3), β = 86·361 (3), γ = 78·181 (3)°, V = 1003·38 (6) Å^3, D_x = 1·345 Mg m^{-3}, Z = 2, λ(Cu $K\alpha$) = 1·54056 Å, μ = 0·82 mm^{-1}, $F(000)$ = 432, room temperature, final R = 0·043 for 2841 observed reflections. The tricyclic compound (1) has the same carbon framework as in the *BCD* rings in a steriod nucleus. Ring *B* adopts a chair while ring *C* has a half-chair conformation. A *trans* relative stereochemistry is observed at the *BC* ring junction while a *cis* hydrinclane is observed for the *CD* junction, the lactone bridge being *cis* to the

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