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The Crystal Structure of 4-*O*-β-D-Galactopyranosyl-L-rhamnitol

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$C_{12}H_{24}O_{10}$, $M_r = 328\cdot32$, monoclinic, $P2_1$, $a = 5\cdot279$ (1), $b = 12\cdot204$ (1), $c = 11\cdot725$ (1) Å, $\beta = 99\cdot70$ (1)° [λ(Cu $K\alpha_1$) = 1·5405 Å], $V = 744\cdot58$ Å^3, $Z = 2$, $D_m = 1\cdot466$, $D_x = 1\cdot464$ g cm^{-3}. The structure was solved with *MULTAN* and refined to $R(F_o^2) = 0\cdot039$ for 1602 reflections. The galactopyranose ring is distorted $^4C_1$ and the conformation of the primary alcohol group is +*sc* (*gauche–trans*). The rhamnitol residue has the straight carbon chain conformation, except for the terminal methyl group. The β-glycosidic torsion angle is −71° and the glycosidic bond is short, 1·384 Å. There is an intramolecular hydrogen bond between the two residues which links a terminal hydroxyl of the rhamnitol to the ring oxygen of the galactose. All the O atoms are involved in the hydrogen bonding which consists of separate finite and infinite chains.

Introduction

The crystals were provided by Professor G. G. S. Dutton of the University of British Columbia. A crystal of dimensions 0·07 × 0·17 × 0·23 mm was used for the data collection with graphite-monochromated Cu $K\alpha$ radiation on a CAD-4 diffractometer. The 4198 intensities in the hkl, $hk\bar{l}$, $h\bar{k}l$ and $h\bar{k}\bar{l}$ octants were measured by θ–2θ scans to $2\theta = 150°$. Absorption corrections were calculated with the program *ABSOR* (Templeton & Templeton, 1973) and a linear absorption coefficient for Cu $K\alpha$ of 10·86 cm^{-1}. The minimum and maximum corrections to F_o^2 were 1·076 and 1·223 respectively. The symmetry-related measurements were then averaged to give 1603 independent reflections, of which 10 had $F_o^2 < 0$. The R value between symmetry-equivalent intensities was 0·016.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971), and 150 E's to the limit of $|E| > 1\cdot5$. The parameters were refined by full-matrix least squares, minimizing $\Sigma\, w(F_o^2 - k^2F_c^2)^2$, with $w^{-1} = \sigma_C^2(F_o^2) + (0\cdot04F_o^2)^2$, where σ_C is from counting statistics. The H atoms were located from a difference synthesis. The non-H and H atoms were refined anisotropically and isotropically respectively, with a Zachariasen isotropic extinction parameter (Coppens & Hamilton, 1970) which refined to 0·91 (9) × 10^4. The 110 reflection was overcorrected for extinction and was omitted from the final cycle of refinement. The final $R = \Sigma\, |F_o^2 - k^2F_c^2/\Sigma\, |F^2|$, and $R_w = [\Sigma\, w(F_o^2 - k^2F_c^2)^2/\Sigma\, w|F_o^2|^2]^{1/2}$ for 1602 reflections were 0·039 and 0·064 respectively ($R = 0\cdot045$ and $R_w = 0\cdot065$ for all 1603 reflections).

The atomic scattering factors for O and C were those tabulated by Doyle & Turner (1968) and those of H were given by Stewart, Davidson & Simpson (1965). The final positional and thermal parameters are given in Tables 1 and 2.† The conformation and the atom numbering of 4-*O*-β-D-galactopyranosyl-L-rhamnitol are shown in Fig. 1. The molecular dimensions for non-H atoms are reported in Fig. 2. Important torsion angles

Table 1. *Positional* (×10^5) *parameters for* 4-*O*-β-D-*galactopyranosyl*-L-*rhamnitol*

Estimated standard deviations are given in parentheses. The O(1) y parameter was used to fix the origin.

	x	y	z
C(1)	43061 (33)	30345 (17)	73857 (13)
C(2)	66857 (35)	23210 (17)	75015 (13)
C(3)	64190 (33)	13834 (17)	83334 (14)
C(4)	57334 (32)	17866 (17)	94897 (13)
C(5)	36288 (33)	26516 (18)	92877 (12)
C(6)	32849 (37)	32454 (20)	103890 (14)
O(1)	45768 (23)	38843	66340 (10)
O(2)	69937 (31)	18548 (16)	64267 (11)
O(3)	87642 (27)	7850 (16)	84989 (12)
O(4)	79430 (25)	21965 (16)	102351 (11)
O(5)	41855 (23)	34847 (14)	84975 (10)
O(6)	11410 (29)	39685 (16)	101795 (13)
C(1′)	−57 (42)	36475 (21)	31308 (15)
C(2′)	5312 (34)	35779 (18)	44460 (14)
C(3′)	17752 (33)	46309 (18)	49878 (13)
C(4′)	23471 (33)	45681 (18)	63102 (13)
C(5′)	27614 (42)	56929 (19)	68941 (16)
C(6′)	53708 (63)	61883 (28)	68782 (29)
O(1′)	−16742 (29)	45337 (18)	27512 (13)
O(2′)	−17719 (27)	33430 (16)	48834 (11)
O(3′)	40793 (27)	48221 (17)	45346 (12)
O(5′)	21921 (38)	56404 (18)	80543 (12)

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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 32484 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

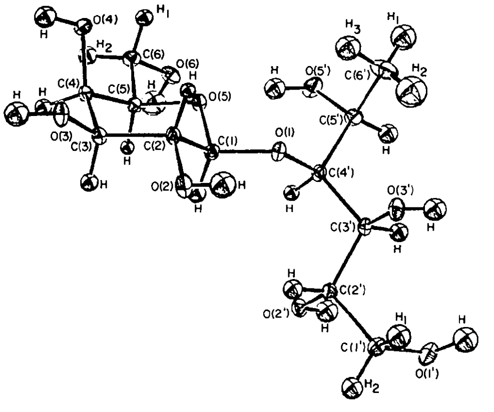

Fig. 1. Conformation of 4-*O*-β-D-galactopyranosyl-L-rhamnitol, with the atomic notation. The thermal ellipsoids are at 20% probability (Johnson, 1976).

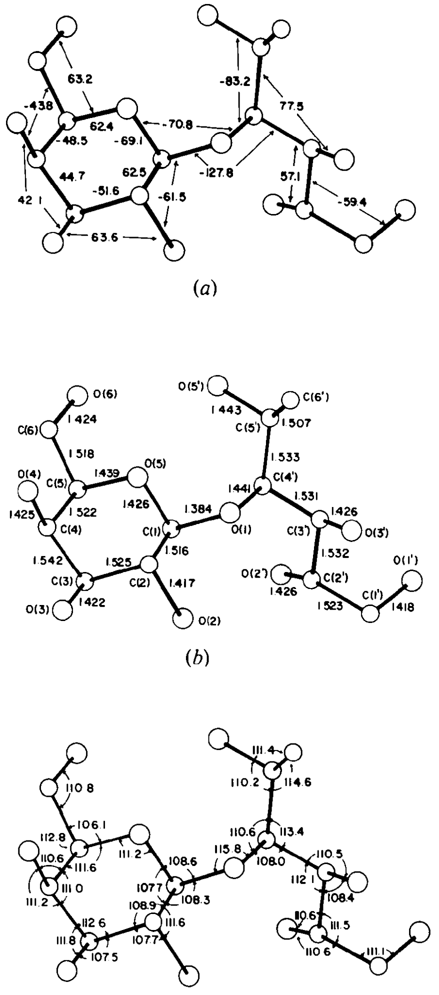

Fig. 2. Molecular dimensions of 4-*O*-β-D-galactopyranosyl-L-rhamnitol. (*a*) Selected torsion angles (°). (*b*) Bond lengths (Å). (*c*) Valence angles(°).

Table 2. *Fractional coordinates* ($\times 10^4$), *isotropic thermal parameters* (Å^2) *and bond distances* (Å) *for the hydrogen atoms*

	x	y	z	B	C,O–H
HC(1)	2776 (46)	2589 (21)	7126 (19)	2·4 (4)	0·98 (2)
HC(2)	8181 (39)	2784 (17)	7807 (16)	1·4 (4)	0·99 (2)
HC(3)	4965 (43)	938 (20)	7934 (19)	2·2 (4)	0·99 (2)
HC(4)	5070 (48)	1136 (20)	9856 (20)	2·2 (4)	0·99 (2)
HC(5)	2039 (41)	2279 (18)	8939 (16)	1·6 (4)	0·98 (2)
HC(61)	4809 (45)	3696 (21)	10686 (19)	2·5 (4)	0·99 (2)
HC(62)	3127 (50)	2675 (23)	11008 (22)	3·3 (5)	1·02 (3)
HO(2)	7196 (61)	2322 (31)	6016 (27)	4·4 (7)	0·77 (4)
HO(3)	8706 (53)	216 (28)	8976 (22)	3·9 (6)	0·90 (3)
HO(4)	8173 (51)	1772 (25)	10780 (24)	3·5 (6)	0·82 (3)
HO(6)	−194 (80)	3562 (66)	10133 (34)	6·0 (8)	0·86 (4)
HC(1′1)	1709 (54)	3758 (25)	2820 (22)	3·7 (5)	1·04 (3)
HC(1′2)	−782 (51)	2965 (24)	2826 (22)	3·0 (5)	0·97 (3)
HC(2′)	1610 (46)	2945 (23)	4667 (20)	2·6 (5)	0·97 (3)
HC(3′)	668 (45)	5225 (21)	4751 (19)	2·5 (4)	0·94 (3)
HC(4′)	869 (40)	4213 (19)	6553 (17)	1·9 (4)	0·98 (2)
HC(5′)	1503 (49)	6205 (24)	6485 (22)	3·0 (5)	0·98 (3)
HC(6′1)	5547 (62)	6851 (32)	7248 (28)	5·0 (7)	0·92 (4)
HC(6′2)	5744 (77)	6163 (37)	6100 (33)	7·2 (1·0)	0·97 (4)
HC(6′3)	6482 (62)	5754 (31)	7402 (26)	4·7 (6)	0·94 (3)
HO(1′)	−674 (62)	5021 (30)	2466 (25)	4·7 (7)	0·90 (4)
HO(2′)	−2840 (59)	3850 (30)	4715 (24)	4·1 (6)	0·84 (3)
HO(3′)	3861 (54)	5361 (28)	4199 (24)	3·6 (6)	0·77 (3)
HO(5′)	2666 (55)	4998 (30)	8328 (23)	3·8 (6)	0·87 (4)

not included in the figure are C(4)–C(5)–C(6)–O(6) −174·4°; C(2)–C(1)–O(1)–C(4′) 172·6°; and C(5′)–C(4′)–O(1)–C(1) 107·7°. The σ's for the bond lengths and angles were 0·002 Å and 0·1° respectively [except 0·004 Å for C(5′)–C(6′), 0·003 Å for C(1′)–O(1′), and 0·2° for O(1′)–C(1′)–C(2′) and O(5′)–C(5′)–C(6′)]. The C–H and O–H bond distances and their estimated standard deviations are included in Table 2.

Discussion

The galactopyranose ring is the normal $^4C_1$ chair (Stoddart, 1971), but the ring distortion is greater than in the α and β galactose structures (Longchambon, Ohannessian & Neuman, 1975; Sheldrick, 1976) and in methyl α-D-galactose hydrate (Gatehouse & Poppleton, 1971), where the ring torsion angles lie in the more commonly observed range of 54 to 64°. This distortion is also shown by the relatively large values for the q_2 and θ puckering parameters (Cremer & Pople, 1975): $q_2 = 0{\cdot}125$ Å, $q_3 = 0{\cdot}564$ Å, $Q = 0{\cdot}577$ Å, $\theta = 12{\cdot}54°$, $\varphi_2 = 45{\cdot}05°$. The O(5)–C(5)–C(6)–O(6) conformational angle of the primary alcohol group is +63° (*i.e. gauche–trans*) as compared with +57° for β-D-galactose (Longchambon, Ohannessian & Neuman, 1975). That of the glycosidic bond O(5)–C(1)–O(1)–C(4′) is −71°, which is the preferred conformation for the methyl β-pyranosides. The deviation from the ideal staggered conformation for the rhamnitol residue is greatest at the CHOH.CH$_3$ terminal, presumably because of the intramolecular hydrogen bond from the hydroxyl to the galactose ring oxygen.

The acetal sequence of bonds, C(5)–O(5)–C(1)–O(1)–C(4′), shows the well established variation in bond lengths which is characteristic of the methyl *β*-pyranosides (*cf.* Jeffrey & Takagi, 1977) and agrees well with the theoretical predictions of Jeffrey, Pople & Radom (1972, 1974). The other C–C and C–O bond lengths show small variations from the mean values of 1·525 and 1·425 Å respectively, which are not significant. Possible exceptions are the long C(3)–C(4) and C(5′)–O(5′) bonds where the differences from the mean values are 8*σ*. The former is associated with the smallest ring torsion angle, but there is no obvious explanation for the latter. The only valence angles of note are those of the ring bonds at O(5) and C(1) which have the characteristic 'smaller' values for a *β*-pyranoside (*cf.* Jeffrey & Takagi, 1977) and that at the linkage oxygen which is also characteristically greater than 110° (*cf.* Arnott & Scott, 1972).

The hydrogen bonding involves all the hydroxyl groups and the ring oxygen. All the hydroxyl oxygens except O(1′) act as both donors and acceptors. The hydrogen-bond structure consists of an infinite chain, ···O(2)–H···O(2′)–H···O(3′)–H···O(2)–H···, and a finite chain, O(1′)–H···O(3)–H···O(6)–H···O(4)–H···O(5′)–H···O(5). The geometry of these chains is illustrated in Figs. 3 and 4, which show the hydrogen bonding and the molecular packing. Table 3 gives the hydrogen-bond distances and angles, with the O–H distances normalized to the neutron diffraction value of 0·96 Å by moving the H atom in the direction of the O–H bond. This permits comparison

Table 3. *Hydrogen-bond distances* (Å) *and angles* (°) *in the structure of* 4-*O*-*β*-D-*galactopyranosyl*-L-*rhamnitol*

Type	H···O*corr.	O···O	O–H···O*corr.
···O–H···O–H···			
O(3)–H···O(6) [x,y,z] to [1 – x, –½ + y, 1 – z]	1·75	2·700 (2)	172
O(2)–H···O(2′) [x,y,z] to [1 + x,y,z]	1·77	2·719 (2)	168
O(3′)–H···O(2) [x,y,z] to [1 – x, ½ + y, 1 – z]	1·80	2·744 (2)	168
O(4)–H···O(5′) [x,y,z] to [1 – x, –½ + y, 2 – z]	1·84	2·772 (2)	164
O(6)–H···O(4) [x,y,z] to [x – 1, y, z]	1·86	2·751 (2)	154
O(2′)–H···O(3′) [x,y,z] to [x – 1, y, z]	1·88	2·814 (2)	165
O–H···O–H···			
O(1′)–H···O(3) [x,y,z] to [1 – x, ½ + y, 1 – z]	1·82	2·757 (2)	163
···O–H···O<			
O(5′)–H···O(5) [x,y,z] to [x,y,z]	1·92	2·849 (2)	161

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

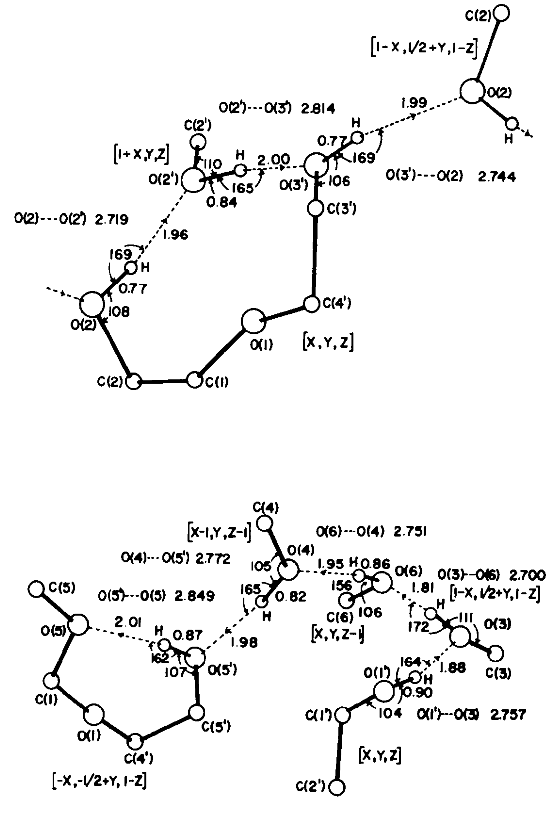

Fig. 3. Hydrogen-bond structure in the crystal structure of 4-*O*-*β*-D-galactopyranosyl-L-rhamnitol. Top: infinite chain ···O(2)H···O(2′)H···O(3′)H···. Bottom: finite chain O(1′)H···O(3)H···O(6)H···O(4)H···O(5′)H···O(5).

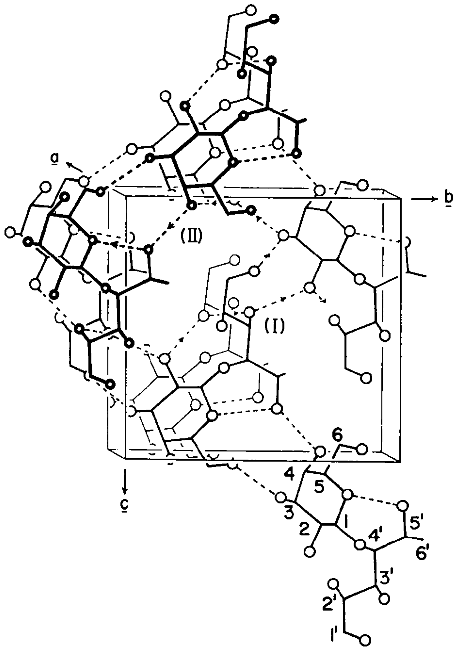

Fig. 4. Hydrogen bonds (dashed lines) and molecular packing in the structure of 4-*O*-*β*-D-galactopyranosyl-L-rhamnitol.

with the more definitive bond distances available from neutron diffraction studies of carbohydrates (*cf.* Jeffrey, Gress & Takagi, 1977). The corrected H···O distances for hydrogen bonds between the hydroxyl groups range from 1·75 to 1·88 Å. This is intermediate between the 1·736 to 1·820 Å range observed in the neutron diffraction studies of the monosaccharides [methyl α-D-manno- and methyl α-D-glucopyranoside (Jeffrey, McMullan & Takagi, 1977); α-D-glucose (Brown & Levy, 1965)], and 1·760 to 1·927 Å in the disaccharides [sucrose (Brown & Levy, 1973); β-maltose monohydrate (Gress & Jeffrey, 1977)]. This could be a consequence of the fact that from the point of view of packing, these molecules have the complexity of a disaccharide, with the acyclic half of the molecule more flexible than in sucrose or maltose. The hydrogen bond to the ring oxygen is longer than between two hydroxyls, but the difference is not as marked as in the methyl pyranoside data referred to above.

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Molecular-Packing Analysis of Some Naphthaquinone and Anthraquinone Structures. The Crystal Structure of 2-Methyl-5,8-dihydroxy-1,4-naphthaquinone

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The structures corresponding to a minimum non-bonded repulsion energy have been shown to be in close agreement with the observed structures for a number of naphthaquinones and anthraquinones. The previously unknown structure of 2-methyl-5,8-dihydroxy-1,4-naphthaquinone was successfully predicted with this procedure. [Crystal data: $C_{11}H_8O_4$, triclinic, a = 7·431 (2), b = 8·479 (2), c = 16·654 (3) Å, α = 87·31 (5), β = 106·8 (1), γ = 114·5 (2)°, Z = 4.]

Introduction

The procedure developed by Williams (1969) for the prediction of molecular crystal structure by the minimization of non-bonded, repulsive packing energy assumes implicitly that the structure is not dominated by specific attractive interactions between molecules. It is, then, essentially applicable to non-polar molecules, but because this procedure is very much faster in terms of computer time than packing-analysis techniques