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THE CRYSTAL AND MOLECULAR STRUCTURE OF *O*-β-D-MANNOPYRANOSYL-(1→4)-α-D-MANNOPYRANOSE (MANNOBIOSE)

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ABSTRACT

The crystal structure of *O*-β-D-mannopyranosyl-(1→4)-α-D-mannopyranose has been determined by direct methods using the MULTAN suite of programs. The space group is $P2_12_12_1$, with 4 molecules in the unit cell with $a = 8.811(4)$, $b = 7.485(2)$, and $c = 21.601(9)$ Å. The structure was refined to R = 0.0511 for 1024 independent reflections measured with CuKα radiation. Difference-Fourier syntheses showed all the hydrogen atoms and a mixture (68:32) of the α and β anom-

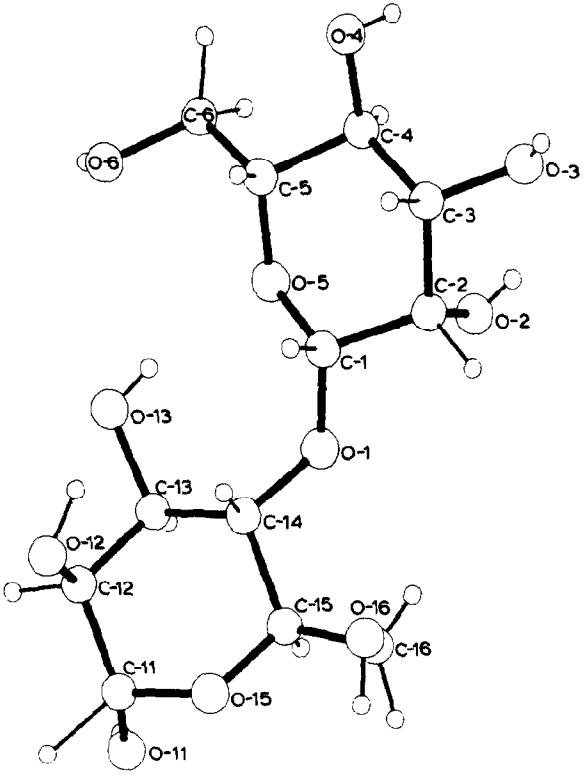

Fig. 1. Molecular conformation and atom numbering in β-D-Man*p*-(1→4)-α-D-Man*p*.

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ers. The sugar residues have the expected $^4C_1$ conformation and their relative orientation is stabilised by an intramolecular hydrogen bond between O-5 and O-13.

INTRODUCTION

The disaccharide β-D-Man*p*-(1→4)-α-D-Man*p* was originally prepared by enzymic digestion of the cell-wall fraction from the green alga *Codium fragile*[1], and purified by chromatographic separation. Numbering of the atoms is shown in Fig. 1. Fig. 2 shows the crystal packing of the molecules.

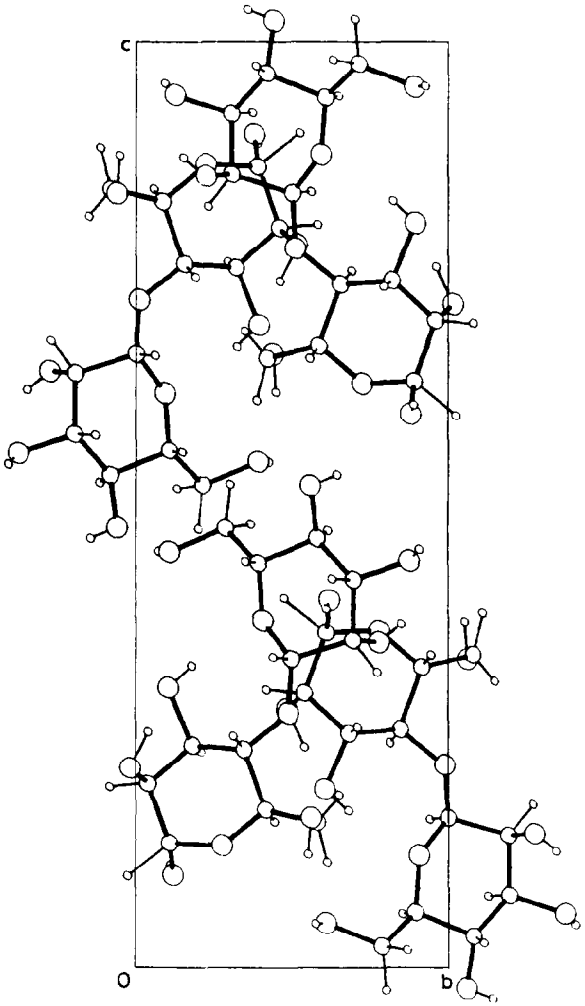

Fig. 2. *a*-Axis projection of the unit cell. Drawn by PLUTO-78[6].

TABLE I

FRACTIONAL ATOM COORDINATES ($\times 10^4$) AND U_{eq} ($A^2 \times 10^4$) OF THE HEAVY ATOMS

Atom	x	y	z	U_{eq}[a]
C-1	7730(8)	4988(9)	3363(3)	304
C-2	7872(8)	6937(9)	3566(3)	322
C-3	8518(9)	6959(10)	4221(3)	382
C-4	7598(9)	5811(10)	4661(3)	355
C-5	7360(8)	3936(9)	4397(3)	321
C-6	6215(10)	2863(10)	4767(3)	477
O-1	7063(5)	4890(6)	2777(2)	350
O-2	6425(6)	7764(7)	3545(2)	411
O-3	8658(6)	8766(7)	4425(2)	496
O-4	8413(7)	5585(7)	5229(2)	494
O-5	6726(5)	4068(6)	3777(2)	350
O-6	6177(7)	1082(7)	4513(2)	551
C-11	7358(11)	1085(12)	1353(3)	575
C-12	7228(8)	402(9)	2007(3)	370
C-13	6601(8)	1803(9)	2433(3)	328
C-14	7608(8)	3461(9)	2392(3)	326
C-15	7514(9)	4152(10)	1726(3)	384
C-16	8410(10)	5802(10)	1594(3)	437
O-11	6168(8)	1198(11)	1003(3)	448
O-21	7694(24)	41(25)	928(8)	648
O-12	8686(6)	−161(7)	2184(2)	533
O-13	6592(6)	1048(6)	3047(2)	433
O-15	8141(7)	2762(7)	1330(2)	568
O-16	9990(6)	5610(8)	1641(2)	526

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

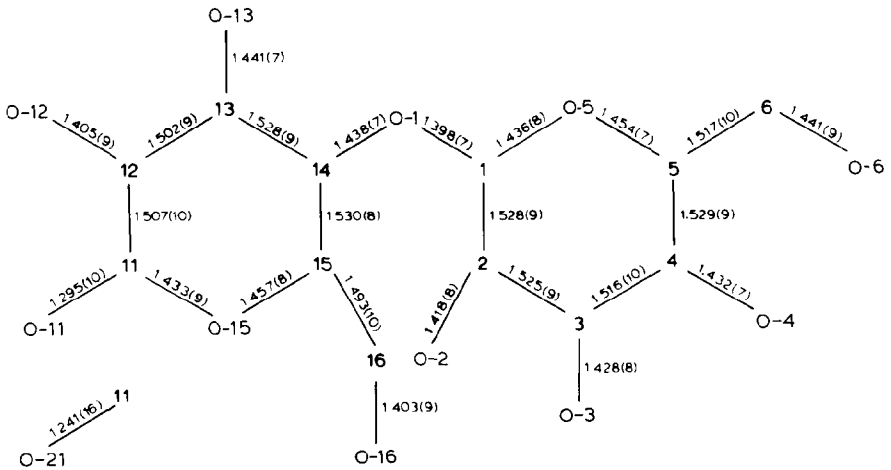

Fig. 3. Intramolecular bond distances (Å) in β-D-Man*p*-(1→4)-α-D-Man*p*.

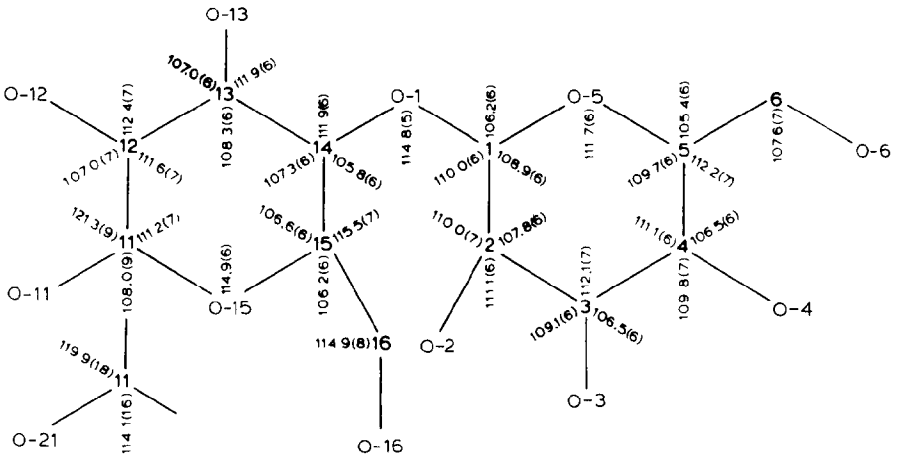

Fig. 4. Bond angles (°) in β-D-Manp-(1→4)-α-D-Manp.

TABLE II

TORSION ANGLES (DEGREES)

	Mannose ring 1	*Mannose ring 2*
C-1–C-2–C-3–C-4	−53.9(8)	−56.2(8)
C-2–C-3–C-4–C-5	51.2(8)	62.7(7)
C-3–C-4–C-5–O-5	−53.0(7)	−63.2(7)
C-4–C-5–O-5–C-1	61.7(7)	60.7(8)
C-5–O-5–C-1–C-3	−66.3(6)	−54.3(9)
O-5–C-1–C-2–C-3	60.3(7)	50.8(9)
O-1–C-1–C-2–O-2	55.6(6)	159.4(8)
O-2–C-2–C-3–O-3	−59.7(7)	65.2(14)
		−57.6(7)
O-3–C-3–C-4–O-4	−67.9(8)	−69.5(7)
O-4–C-4–C-5–C-6	71.2(7)	59.1(8)
C-4–C-5–C-6–O-6	−175.1(6)	65.3(8)
O-5–C-5–C-6–O-6	65.8(7)	−52.8(7)
Inter-ring values		
O-5–C-1–O-1–C-14	−96.1(6)	
C-2–C-1–O-1–C-14	145.8(6)	
C-1–O-1–C-14–C-13	95.1(6)	
C-1–O-1–C-14–C-15	−148.1(6)	

EXPERIMENTAL

Crystals were grown by slow evaporation of a solution in aqueous propan-2-ol. A crystal (0.26 × 0.14 × 0.12 mm) was sealed in a Lindemann glass capillary

and set on a Nonius CAD-4F diffractometer. Unit-cell parameters were calculated as $a = 8.811(4)$, $b = 7.485(2)$, and $c = 21.604(9)$ Å from measurements of θ for 45 indepeiident reflections. V = 1424.8 Å at 293K, and the space group is $P2_12_12_1$ with a calculated density of 1.596 $g.cm^{-3}$. The linear absorption coefficient μ (CuKα) is 1.13 cm^{-1}. Nickel-filtered CuKα radiation (λ = 1.5418 Å) was used to collect 4617 intensity measurements for $2\theta < 140°$, of which 3362 had $I > 3\sigma(I)$. These were merged (merging R = 0.08) to give 1024 unique reflections. The reflection $-2\ -1$ 0 was measured every hour of exposure time (75 measurements) with an average value of 6386 counts and a standard deviation of the distribution = 150 (2.3%). These measurements showed no sign of any crystal deterioration. No absorption corrections were applied.

DISCUSSION

Structure determination. — The structure was solved by direct methods using the MULTAN-80[2] suite of programs. A Fourier synthesis, based on the phases produced for the set with the highest combined figure of merit, showed the locations of all the non-hydrogen atoms. These were refined isotropically, using the SHELX suite of programs[3], and then anisotropically to a value of R = 0.116. The positions of 11 hydrogen atoms were found from a difference-Fourier synthesis and, after two further cycles of anisotropic SFLS refinement (no refinement of the hydrogens), the remaining hydrogen positions were found. At this stage, it became evident that the structure included both α and β anomers, a difference-Fourier synthesis showing a large electron density peak in an appropriate position for the β anomer oxygen-atom. Calculations indicated a ratio of 68:32 for the α and β forms, and further refinement, including both oxygen atoms and their associated hydrogen atoms with the specified occupancy, together with anisotropic refinement of the overall scale, reduced the discrepancy factor to R = 0.051. In the final cycle of SFLS refinement, the maximum shift/e.s.d. was 0.113 and the average shift/e.s.d. 0.011. The final difference-Fourier synthesis showed maximum and minimum electron densities of 0.23 and -0.24 e/Å^3, respectively.

Table I lists the positional parameters of the heavy atoms and the U_{eq} values. Hydrogen atom coordinates, anisotropic thermal vibration parameters, and a Table of observed and calculated structure factors have been deposited*.

Molecular geometry. — Bond distances are shown in Fig. 3 and bond angles in Fig. 4. Torsion angles are given in Table II. The average C–C bond-length is 1.518 Å, and the average C–O (excluding C-1–O-1) bond-length is 1.432 Å although both C-5–O-5 bonds are longer than the mean. The anomeric bond (C-1–O-1) at the glycosidic junction is 1.398 Å, in the normal range for an equatorial link-

*The vibrational parameters U_{ij} of the heavy atoms, the coordinates and U_{iso} values of the H atoms, and a list of F_o and F_c structure factors are deposited with, and can be obtained from: Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/288/*Carbohydr. Res.*, 132 (1984) 1–6.

age. Internal C–C–C ring angles are close to the tetrahedral value (range 107.3–112.1°, mean 109.7°), but the external C–C–C angles are significantly larger [112.2(7)° and 115.5(7)°].

Both residues have the expected $^4C_1$ conformation with, for the reducing oxygen atom, the α and β anomers being found in a ratio of 2:1 as in the crystal structure of *O*-α-D-mannopyranosyl-(1→3)-*O*-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-α-D-glucopyranose[4].

The structural parameters of mannobiose are of interest in relation to the polymorphic forms of mannan I and mannan II, both of which occur in Nature[5]. Further detailed consideration of the molecular geometry of mannobiose and its relationship to the parent polysaccharide, and to such related compounds as cellodextrins, mannotriose, and other mannose-containing oligosaccharides and polysaccharides, will be given in a forthcoming paper.

ACKNOWLEDGMENTS

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