Carbohydrate Research, 60 (1978) 219–228

AN X-RAY CRYSTALLOGRAPHIC STUDY OF α-D-ALLOPYRANOSYL α-D-ALLOPYRANOSIDE · $CaCl_2 \cdot 5H_2O$ (A PENTADENTATE COMPLEX)

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(Received December 2nd, 1976; accepted for publication April 26th, 1977)

ABSTRACT

Three-dimensional, single-crystal, X-ray diffraction methods were used to determine the structure of the calcium chloride complex of α-D-allopyranosyl α-D-allopyranoside. The crystal is monoclinic with cell dimensions: $a = 16.262(5)$, $b = 8.345(5)$, $c = 8.298(5)$Å, $\beta = 98.428(5)°$, and $z = 2$. The space group is $P2_1$. The structure was solved by three-dimensional Patterson and Fourier methods, and was refined by least-squares techniques to give a conventional discrepancy factor of $R = 0.026$; 2435 diffractometer-read reflections were used. The cation was found to be in 9-fold co-ordination to O-1, O-2, O-3, O-2′, O-3′, and four water molecules.

INTRODUCTION

Numerous complexes of sugars with salts are known, particularly with calcium chloride[1]; the structures of about a dozen such complexes have been determined by X-ray crystallographic analysis[2–8]. In solution, a sugar or a polyol forms a reasonably strong complex with cations if it contains a sequence of an axial, an equatorial, and an axial hydroxyl group on a six-membered ring, or a sequence of three *cis* hydroxyl groups on a five-membered ring[9]. It is reasonable to expect that, in the crystalline complex of such a sugar or polyol, the cation would be found co-ordinated to the same three oxygen atoms; this proved to be true in the four cases so far investigated, namely, β-D-mannofuranose · $CaCl_2 \cdot 4H_2O$[3], methyl β-D-mannofuranoside · $CaCl_2 \cdot 3H_2O$[6], methyl α-D-*glycero*-D-*gulo*-heptopyranoside · $CaCl_2 \cdot H_2O$[6], and *epi*-inositol · $SrCl_2 \cdot H_2O$[8]. When the sugar does not contain three oxygen atoms in the configuration favourable for complex formation, the cation is co-ordinated to fewer than three oxygen atoms of each sugar molecule in the crystal.

We have been interested in finding examples of a cation that is co-ordinated to more than three oxygen atoms of a sugar. It appeared that this could occur in a disaccharide in which each component sugar has an axial–equatorial–axial sequence of three oxygen atoms. Hence, with the kind assistance of Dr. A. C. Richardson, we synthesized α-D-allopyranosyl α-D-allopyranoside ("*allo*,*allo*-trehalose")[10]. The sugar did not crystallize, but it gave a beautifully crystalline complex with calcium chloride; even its 4,6:4′,6′-di-*O*-benzylidene derivative gave a calcium chloride complex. The n.m.r. spectrum of the disaccharide showed that the signal of H-2 shifted downfield considerably on addition of calcium chloride, and those of H-1 and H-3 to a lesser extent, indicative of complex formation at O-1, O-2, and O-3. However, the spectrum did not allow a decision on whether there exists in solution a pentadentate complex or a rapid equilibrium between the two possible tridentate complexes, each involving only one half of the disaccharide. The electrophoretic mobility (relative to *cis*-inositol in 0.2M calcium acetate containing 0.2M acetic acid) was considerably greater (0.55) than that of methyl α-D-allopyranoside (0.20); this suggests that a pentadentate complex is formed. We therefore carried out an X-ray crystallographic study which proved that the complex is, indeed, pentadentate in the crystal.

EXPERIMENTAL

Octa-acetate of α-D-allopyranosyl α-D-allopyranoside. — α-D-Allopyranosyl α-D-allopyranoside was prepared according to the procedure of Richardson and his co-workers[10], and was characterized as its octa-acetate. Acetylation was achieved with excess of acetic anhydride and pyridine at 100° for 90 min to yield, after evaporation of the solvents under reduced pressure, a brown syrup which crystallized on standing. The product was recrystallized from ethanol to give, as colourless needles, α-D-allopyranosyl α-D-allopyranoside octa-acetate, m.p. 192–193°, $[\alpha]_D^{22}$ +149.5° (*c* 0.89, methanol).

Anal. Calc. for $C_{28}H_{38}O_{19}$: C, 49.6; H, 5.8. Found: C, 49.8; H, 5.6.

Calcium chloride complex of α-D-allopyranosyl α-D-allopyranoside. — A solution of anhydrous calcium chloride (35 mg, 1 equiv.) and α-D-allopyranosyl α-D-allopyranoside (108 mg) in water (4 ml) was allowed to evaporate under reduced pressure in a desiccator. The product was dissolved in boiling ethanol, and acetone was carefully added. After 18 h, the mixture yielded, as colourless crystals, the complex, m.p. 240° (dec.), $[\alpha]_D^{22.5}$ +115° (*c* 1.1, water).

Anal. (air-dried sample). Calc. for $C_{11}H_{22}O_{11} \cdot CaCl_2 \cdot 5H_2O$: C, 26.6; H, 5.9. Found: C, 26.7; H, 5.9.

Crystal data. — Oscillation and Weissenberg photographs show the crystals to be monoclinic. Systematic absences among the reflections indicate the space group to be $P2_1$. The crystal used for data collection was prismatic, elongated parallel to [1 -1 0] and [-1 -1 0] — the forms present being [0 0 1], [1 0 0], [1 -1 0], and [-1 -1 0] — with a crystal volume of 0.42 cm^{-3}. Single-crystal diffractometry yielded the following lattice constants: $a = 16.262(5)$, $b = 8.346(5)$, $c = 8.298(5)$Å, $\beta = 98.428°(5)$. There are two formula units per unit cell.

Intensity data. — Intensity measurements were carried out on a computer-controlled Siemens A.E.D. diffractometer. Integrated intensities for 2435 independent reflections (θ up to 70°) were measured using CuKα radiation and a $\theta/2\theta$ scan technique[11]. These intensities were corrected for background and absorption[12], and

TABLE I

PARAMETERS FOR NON-HYDROGEN ATOMS AND THEIR STANDARD DEVIATION[a]

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca	2852.1(3)	2456.3(7)	10877.6(2)	15.2(2)	55.3(8)	51.6(7)	−2.2(4)	1.2(3)	10.6(8)
Cl-1	5257.9(5)	4101 (1)	5324 (1)	26.3(3)	107 (1)	108 (1)	−4.0(6)	12.0(5)	−24 (1)
Cl-2	1510.2(5)	7351 (1)	714 (1)	35.3(3)	53 (1)	168 (2)	−0.8(6)	10.0(6)	25 (1)
O-1	2141 (1)	3548 (3)	8150 (2)	16.2(7)	77 (3)	60 (3)	−4 (1)	5 (1)	14 (3)
O-2	1417 (1)	3664 (3)	10792 (3)	25.9(8)	64 (3)	76 (3)	−3 (1)	4 (1)	−8 (3)
O-3	1686 (1)	781 (3)	9663 (3)	23.3(8)	56 (3)	100 (3)	−0 (1)	−4 (1)	13 (3)
O-4	375 (1)	−942 (3)	7657 (3)	36 (1)	75 (3)	101 (4)	−21 (2)	−4 (2)	2 (3)
O-5	880 (1)	3124 (3)	6389 (3)	20.7(9)	65 (3)	76 (3)	−1 (1)	−2 (1)	6 (3)
O-6	752 (2)	1547 (3)	3376 (3)	33 (1)	109 (4)	79 (3)	11 (2)	12 (1)	19 (3)
O-2′	3526 (1)	1950 (3)	8338 (3)	26.0(9)	62 (3)	106 (4)	6 (1)	13 (1)	18 (3)
O-3′	3616 (1)	4780 (3)	9957 (2)	25.3(8)	98 (4)	60 (3)	−13 (2)	5 (1)	8 (3)
O-4′	4089 (1)	7653 (3)	8510 (3)	27.3(8)	77 (4)	120 (4)	−12 (2)	16 (1)	−16 (3)
O-5′	2470 (1)	5280 (3)	6098 (2)	24.0(8)	66 (3)	66 (3)	−4 (1)	4 (1)	17 (3)
O-6′	2887 (2)	8263 (3)	4705 (3)	35 (1)	129 (5)	131 (4)	−3 (2)	7 (2)	65 (4)
WO-1	4236 (1)	2146 (3)	12446 (3)	26.0(8)	93 (4)	114 (4)	2 (2)	−6 (1)	9 (3)
WO-2	2427 (1)	1268 (3)	13272 (3)	28 (1)	102 (4)	98 (3)	8 (2)	12 (2)	35 (3)
WO-3	2914 (2)	4829 (3)	12783 (3)	41 (1)	107 (4)	81 (3)	−3 (2)	14 (2)	−2 (3)
WO-4	3316 (2)	−541 (3)	10865 (3)	36 (1)	105 (4)	122 (4)	1 (2)	9 (2)	−14 (3)
WO-5	5145 (2)	1184 (4)	7824 (3)	35 (1)	138 (5)	117 (4)	22 (2)	11 (2)	14 (4)
C-1	1263 (2)	3831 (4)	7832 (4)	17 (1)	57 (4)	73 (4)	−0 (2)	−0 (2)	9 (4)
C-2	905 (2)	3208 (4)	9317 (4)	16 (1)	72 (5)	75 (5)	1 (2)	2 (2)	−7 (4)
C-3	854 (2)	1393 (4)	9344 (4)	21 (1)	70 (5)	73 (5)	−8 (2)	9 (2)	5 (4)
C-4	416 (2)	780 (4)	7719 (4)	18 (1)	72 (5)	85 (5)	−8 (2)	4 (2)	2 (4)
C-5	849 (2)	1410 (4)	6338 (4)	18 (1)	63 (5)	82 (5)	−4 (2)	3 (2)	5 (4)
C-6	373 (2)	979 (5)	4699 (4)	29 (1)	100 (5)	81 (5)	−13 (2)	4 (2)	3 (4)
C-1′	2573 (2)	3757 (4)	6791 (4)	23 (1)	64 (5)	61 (4)	−5 (2)	12 (2)	5 (4)
C-2′	3482 (2)	3405 (4)	7405 (4)	23 (1)	63 (4)	67 (4)	2 (2)	11 (2)	12 (4)
C-3′	3917 (2)	4775 (4)	8425 (4)	19 (1)	81 (5)	79 (5)	−2 (2)	12 (2)	11 (4)
C-4′	3740 (2)	6356 (4)	7530 (4)	20 (1)	65 (4)	69 (4)	−5 (2)	9 (2)	1 (4)
C-5′	2811 (2)	6609 (4)	7115 (4)	21 (1)	59 (5)	87 (5)	−1 (2)	11 (2)	7 (4)
C-6′	2557 (2)	8130 (4)	6194 (5)	28 (1)	78 (5)	148 (6)	7 (2)	12 (2)	24 (5)

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[a] The values have been multiplied by 10^4. The temperature factor is in the form: $T = \exp - [(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

TABLE II

HYDROGEN-ATOM PARAMETERS (MULTIPLIED BY 10^3)

	x/a	y/b	z/c
H-1	123	503	764
H-2	31	365	914
H-3	55	107	1015
H-4	−17	112	745
H-5	144	103	642
H-6	38	−25	467
H-7	−19	143	459
H-8	137	473	1072
H-9	171	−30	1007
H-10	81	−132	842
H-11	56	258	301
H-1′	234	302	582
H-2′	374	335	628
H-3′	452	457	844
H-4′	395	615	660
H-5′	256	659	820
H-6′	195	818	598
H-7′	273	920	687
H-8′	402	141	819
H-9′	409	529	1070
H-10′	463	750	862
H-11′	343	861	504
W-1–H-1	437	285	1334
W-1–H-2	428	115	1280
W-2–H-1	190	138	1310
W-2–H-2	282	27	1362
W-3–H-1	269	499	1396
W-3–H-2	260	580	1243
W-4–H-1	360	−100	1000
W-4–H-2	380	13	1114
W-5–H-1	550	196	761
W-5–H-2	499	59	712

were converted into a set of relative $|F|$'s through the application of Lorentz-polarization factors. In the absorption correction, a linear absorption coefficient of 52.573 cm^{-1} was used; this value was obtained from the calculated density (1.62 $g.cm^{-3}$) and the mass absorption coefficients for CuKα radiation[13].

Structure determination and refinement. — A three-dimensional Patterson synthesis was interpreted to give the location of the calcium and the two chloride ions. All the remaining atoms were located by using Fourier techniques. The model structure was then refined by using a block-diagonal matrix least-squares program[14] with anisotropic temperature factors. The hydrogen atoms were assigned thermal parameters equal to those of the atoms with which they were most closely associated. The hydrogen-atom positional parameters were included in the block-diagonal refinement. For the final stages of the refinement, a full-matrix least-squares program was used[15] with anisotropic temperature factors and an isotropic extinction parameter[16]. Individual weights w_{hkl}, equal to the reciprocal of the square of the estimated standard deviation of the measurement, were used throughout the refinement, and the function that was minimized was $\Sigma_{hkl}(|F^o_{hkl}| - k|F^c_{hkl}|)^2$. Unobserved reflections are not included if their calculated value is less than the observed value. The hydrogen-atom parameters were not included in the refinement at this stage. A final, conventional R factor of 0.026 (omitting unobserveds) was obtained ($R = 0.028$ with unobserveds included) with a goodness-of-fit index $(\Sigma w\Delta^2/\text{n-p}) = 2.86$. The scattering factors used were those of Doyle and Turner[17], and the anomalous scattering factors for Ca^{2+}, Cl^-, and O were taken from the data of Cromer[18].

DISCUSSION

The main interest in the structure lies in the way in which the calcium ion is co-ordinated to *allo,allo*-trehalose, and in any conformational changes caused in the sugar by this co-ordination. To recognize the latter, a comparison with the structure of crystalline *allo,allo*-trehalose would be desirable, but this structure is not known. Useful comparisons can, however, be drawn with α,α-trehalose[19] (α-D-glucopyranosyl α-D-glucopyranoside), the calcium bromide complex of α,α-trehalose[7], and various monosaccharides.

Individual molecules of *allo,allo*-trehalose have two-fold axes of symmetry, the two glucose moieties being chemically equivalent. In the crystal structure of the calcium chloride complex, however, the two halves are not equivalent; some of the bond lengths and angles show differences considerably larger than the experimental error. In Tables III–V, the data for the two moieties (unprimed and primed) are juxtaposed to allow easy comparison. The two hydroxymethyl groups occur in different conformations: in one, the hydroxyl group is antiperiplanar, in the other it is *gauche*, to the C-5–C-4 bond. The arrangement of the chloride ions and the water molecules also lacks two-fold symmetry. The different conformations of the two halves of the molecule are caused by the packing in the crystal lattice. Similar conformational differences were found between the two halves of crystalline α,α-trehalose[19], but the calcium bromide complex of α,α-trehalose appears to have a two-fold axis[7].

Five oxygen atoms of the sugar are involved in co-ordination with the calcium ion, these being O-1, O-2, O-3, O-2′ and O-3′ (Fig. 1). Four of the water molecules are also co-ordinated with the ion through their oxygen atoms, labelled WO-1, WO-2, WO-3, and WO-4, giving the calcium ion a total of nine co-ordinating oxygen atoms. The co-ordination polyhedron is illustrated in Fig. 2. Nine-fold co-ordination of the calcium ion is unusual; it has not been found in other sugar–calcium complexes, but it occurs in the complex of *epi*-inositol with strontium chloride[8]. The Ca–O distances, listed in Table III, range from 2.410 to 2.614 Å, with an average value of 2.507 Å, indicating that all these associations are of approximately equal strength.

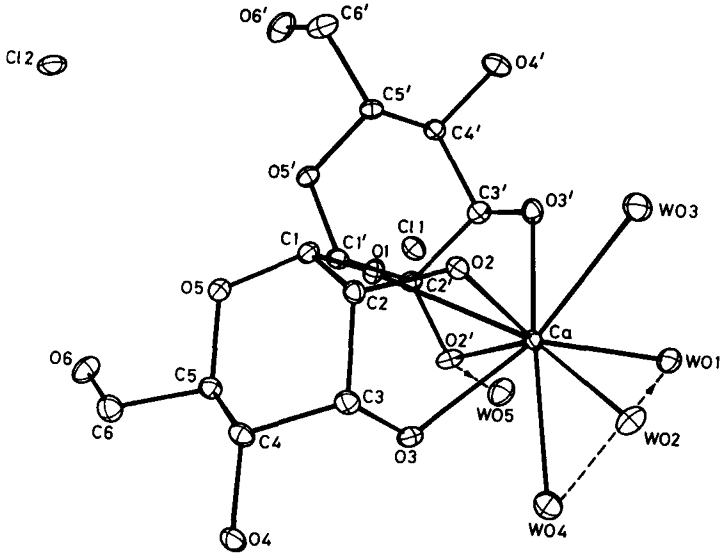

Fig. 1. ORTEP plot of calcium complex of α,α-*allo*,*allo*-trehalose, showing intramolecular hydrogen-bonding, with arrows denoting the donor direction.

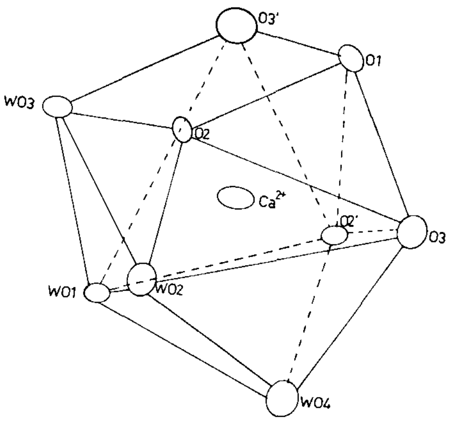

Fig. 2. ORTEP plot showing co-ordination polyhedron surrounding the Ca^{2+} ion.

The Ca–O distances are somewhat longer than those found in the common eight-fold co-ordination (2.35–2.55 Å) which, in turn, are longer than those in seven-fold co-ordination[4,7] (2.32–2.48 Å). It is interesting to compare the structure of the *allo*,*allo*-trehalose complex, in which the calcium ion is co-ordinated to the oxygen atoms of one molecule only, with that of α,α-trehalose, calcium bromide monohydrate[7]. This sugar does not provide an *ax-eq-ax* sequence of oxygen atoms and, in the crystal structure, the calcium ion is co-ordinated to the hydroxyl groups of four molecules.

Fig. 3 shows how the complexes pack together in the unit cell.

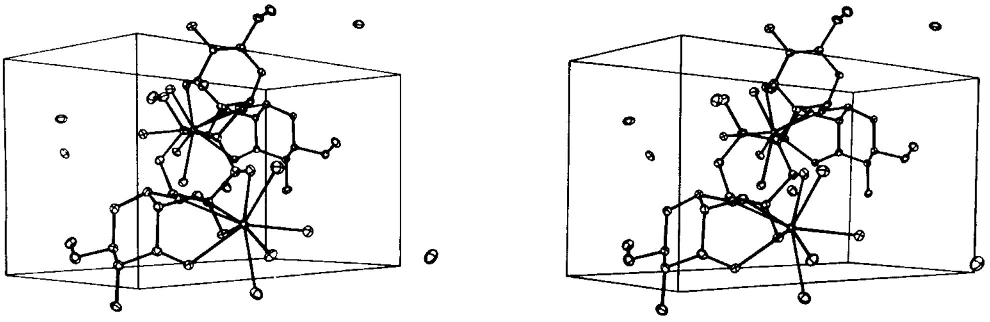

Fig. 3. ORTEP plot of calcium complex of α,α-*allo*,*allo*-trehalose, showing the packing arrangement of the complex in the unit cell.

TABLE III

INTERATOMIC DISTANCES AND STANDARD DEVIATIONS (ÅNGSTROMS)

C-1–C-2	1.529(4)	C-1′–C-2′	1.520(4)	Ca–O-1	2.554(5)
C-2–C-3	1.517(4)	C-2′–C-3′	1.533(5)	Ca–O-2	2.533(5)
C-3–C-4	1.518(4)	C-3′–C-4′	1.521(5)	Ca–O-3	2.452(5)
C-4–C-5	1.524(4)	C-4′–C-5′	1.514(4)	Ca–O-2′	2.548(5)
C-5–O-5	1.432(4)	C-5′–O-5′	1.454(4)	Ca–O-3′	2.483(5)
O-5–C-1	1.397(4)	O-5′–C-1′	1.395(4)	Ca–WO-1	2.443(5)
C-1–O-1	1.433(3)	C-1′–O-1	1.425(3)	Ca–WO-2	2.410(5)
C-2–O-2	1.428(4)	C-2′–O-2′	1.436(4)	Ca–WO-3	2.527(5)
C-3–O-3	1.434(4)	C-3′–O-3′	1.427(4)	Ca–WO-4	2.614(5)
C-4–O-4	1.440(4)	C-4′–O-4′	1.421(4)		
C-5–C-6	1.507(4)	C-5′–C-6′	1.508(5)		
C-6–O-6	1.416(4)	C-6′–O-6′	1.422(5)		

The bond lengths are listed in Table III; the mean C–C bond distance is 1.519 Å, and the mean C–O bond distance is 1.426 Å. These values are not significantly different from those met with in other pyranoid structures, except for the O-5–C-1 lengths which are unusually short (1.395 and 1.397 Å). Jeffrey and his co-workers[20] observed that the anomeric C–O bonds in aldoses are shorter than the other C–O bonds, owing to their partial double-bond character caused by a drift of electrons towards the ring oxygen atom. In our case, the electron attraction of the cation gives rise to the opposite effect: the C-1–O-1 bonds are of normal length, but the C-1–O-5 bonds are considerably shortened.

The bond angles are listed in Table IV; only the angle at O–5 is unusual, being larger than the value of ~114° usually found in pyranoses.

It has been observed previously[7,8,21] that chelation by oxygen atoms to a cation causes a decrease in the spacing between those oxygen atoms. The data in Table VI show that the distances between O-1 and O-2, and between O-2 and O-3, are shorter than the usual distance between vicinal oxygen atoms on a pyranoid ring. Reduction of this distance requires a flattening of the ring, which is also recognisable

TABLE IV

INTERATOMIC ANGLES AND STANDARD DEVIATIONS (DEGREES)

C-1–C-2–C-3	112.3(3)	C-1′–C-2′–C-3′	112.8(3)
C-2–C-3–C-4	110.1(3)	C-2′–C-3′–C-4′	109.8(2)
C-3–C-4–C-5	110.1(2)	C-3′–C-4′–C-5′	110.0(2)
C-4–C-5–O-5	109.9(3)	C-4′–C-5′–O-5′	108.0(2)
C-5–O-5–C-1	117.1(2)	C-5′–O-5′–C-1′	116.3(2)
O-5–C-1–C-2	111.8(2)	O-5′–C-1′–C-2′	111.6(2)
C-1–C-2–O-2	110.9(2)	C-1′–C-2′–O-2′	108.3(2)
O-2–C-2–C-3	106.3(3)	O-2′–C-2′–C-3′	110.5(2)
C-2–C-3–O-3	107.8(3)	C-2′–C-3′–O-3′	107.7(2)
O-3–C-3–C-4	110.5(3)	O-3′–C-3′–C-4′	111.6(3)
C-3–C-4–O-4	112.4(3)	C-3′–C-4′–O-4′	110.5(2)
O-4–C-4–C-5	110.0(3)	O-4′–C-4′–C-5′	108.9(3)
C-4–C-5–C-6	111.3(3)	C-4′–C-5′–C-6′	115.0(3)
C-6–C-5–O-5	106.0(3)	C-6′–C-5′–O-5′	107.1(2)
C-5–C-6–O-6	113.3(3)	C-5′–C-6′–O-6′	113.3(3)
O-1–C-1–O-5	113.3(2)	O-1–C-1′–O-5′	113.2(2)
C-2–C-1–O-1	106.4(2)	C-2′–C-1′–O-1	106.2(2)
C-1–O-1–C-1′	115.4(2)		

TABLE V

TORSIONAL ANGLES AND STANDARD DEVIATIONS (DEGREES)

C-5–O-5–C-1–C-2	−52.6(3)	C-5′–O-5′–C-1′–C-2′	−54.9(3)
O-5–C-1–C-2–C-3	48.5(4)	O-5′–C-1′–C-2′–C-3′	47.7(3)
C-1–C-2–C-3–C-4	−51.0(4)	C-1′–C-2′–C-3′–C-4′	−49.1(3)
C-2–C-3–C-4–C-5	55.0(4)	C-2′–C-3′–C-4′–C-5′	55.4(3)
C-3–C-4–C-5–O-5	−56.3(3)	C-3′–C-4′–C-5′–O-5′	−59.4(3)
C-4–C-5–O-5–C-1	+56.9(3)	C-4′–C-5′–O-5′–C-1′	61.0(3)
O-1–C-1–C-2–O-2	43.1(3)	O-1–C-1′–C-2′–O-2′	46.5(3)
O-2–C-2–C-3–O-3	−51.8(3)	O-2′–C-2′–C-3′–O-3′	−48.8(3)
C-3–C-2–C-1–O-1	−75.7(3)	C-3′–C-2′–C-1′–O-1	−76.1(3)
C-2–C-1–O-1–C-1′	168.4(2)	C-2′–C-1′–O-1–C-1	179.8(2)
O-5–C-1–O-1–C-1′	45.1(3)	O-5′–C-1′–O-1–C-1	57.1(3)
O-6–C-6–C-5–C-4	179.8(3)	O-6′–C-6′–C-5′–C-4′	57.3(4)
O-6–C-6–C-5–O-5	60.2(4)	O-6′–C-6′–C-5′–O-5	−62.8(3)
O-3–C-3–C-4–O-4	59.0(4)	O-3′–C-3′–C-4′–O-4′	56.6(4)

from the unusually small torsional angles around the C-1–C-2 and C-2–C-3 bonds in the ring (Table V). The distances between the *syn*-axial O-1 and O-3 atoms (2.780 and 2.830 Å) are also shorter than those found between *syn*-axial oxygen atoms in other (uncomplexed) sugars, *e.g.*, 2.94 Å in methyl α-D-altropyranoside[22] and 2.96 Å in *epi*-inositol[23]. The distances between O-1, O-2, and O-3 are closely similar to those in β-D-mannofuranose · $CaCl_2$ · $4H_2O$[3], methyl β-D-mannofuranoside · $CaCl_2$ · $3H_2O$[6], and methyl α-D-*glycero*-D-*gulo*-heptopyranoside · $CaCl_2$ · H_2O[6].

The conformation around the bridging oxygen atom, as seen from the torsional

TABLE VI

HYDROGEN-BOND DISTANCES AND ANGLES[a]

i	*j*	*k*	*D(ik)(Å)*	*<ijk*
Cl-1	H-11(*d*)	O-6′(*d*)	3.101	153.9°
Cl-1	W-1–H-1(*b*)	WO-1(*b*)	3.156	154.7°
Cl-2	H-8(*b*)	O-2(*b*)	3.082	168.9°
O-4	H-11(*c*)	O-6(*c*)	2.833	149.4°
O-6	W-2–H-1(*b*)	WO-2(*b*)	2.749	163.6°
O-5′	W-3–H-1(*b*)	WO-3(*b*)	2.969	171.9°
WO-1	W-4–H-2	WO-4	2.901	143.0°
WO-4	W-4–H-1	O-4′(*a*)	2.896	166.9°
WO-5	H-8′	O-2′	2.802	157.4°

NON-BONDED O . . . O DISTANCES LESS THAN 3.2Å

i	*j*	*D(ij)(Å)*	*i*	*j*	*D(ij)(Å)*
O-1	O-5	2.364	O-1	O-5′	2.354
O-3	O-1	2.780	O-3′	O-1	2.830
O-3	O-2	2.642	O-3′	O-2′	2.711
O-2	O-1	2.638	O-2′	O-1	2.602
O-3	O-4	2.888	O-3′	O-4′	2.838
O-5	O-6	2.806	O-5′	O-6′	2.868
O-2	WO-2	3.153	O-2′	WO-4	3.008
O-2	WO-3	2.902	O-1	WO-5	2.802
O-3	WO-2	3.087	O-3′	WO-1	3.083
O-3	WO-4	2.910	O-3′	WO-3	2.754
WO-1	WO-3	3.145	WO-2	WO-3	3.117
WO-2	WO-4	3.034	O-6	O-2(*b*)	3.093

[a] Symmetry codes: (*a*) x, −1 + y, z; (*b*) x, y, −1 + z; (*c*) −x, −1/2 + y, 1 − z; (*d*) 1−x, −1/2 + y, 1 − z.

angles (Table V), is close to the fully extended one in which C-2, C-1, O-1, C-1′, and C-2′ form a planar zig-zag. This is the usual conformation of methyl glycopyranosides, and is the one found in α,α-trehalose[19]. There is no reason to doubt that this would also be the conformation in *allo,allo*-trehalose. Fortuitously, this is also the conformation which places the five oxygen atoms in suitable position for co-ordination to the cation. The only conformational changes caused by complex formation in *allo,allo*-trehalose are therefore the shortening of the C-1–O-5 bond and the decrease in the distances between the oxygen atoms involved in complex formation.

Details of hydrogen bonding are given in Table VI. Non-bonded O...O distances less than 3.2 Å are also given there. Hydrogen bonding within the co-ordination shell of the calcium ion is indicated in Fig. 1.

ACKNOWLEDGMENTS

The authors thank Dr. A. C. Richardson (Queen Elizabeth College, London) for a sample of α-D-allopyranosyl α-D-allopyranoside and for details of its synthesis in advance of publication, and also D. C. Craig (School of Chemistry, University of New South Wales, Kensington) for making available computing programs used in the crystallographic analysis.

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