Carbohydrate Research, 145 (1985) 13–24
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CRYSTAL STRUCTURE AT 87 K OF SODIUM α-L-GULURONATE DIHYDRATE

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(Received April 27th, 1985; accepted for publication, July 5th, 1985)

ABSTRACT

X-Ray data collected at 87 K showed crystals of sodium α-L-guluronate dihydrate ($C_6H_9O_7Na \cdot 2\ H_2O$) to be orthorhombic, $P2_12_12_1$ with $a = 7.591(2)$, $b = 18.884(5)$, $c = 6.842(2)$ Å, and $Z = 4$. The structure was solved by direct methods, and full-matrix least-squares refinement based on 1587 F_o yielded $R = 0.043$ and $R_w = 0.033$. The structure analysis indicates partial anomeric disorder with $\alpha:\beta$ ~90:10. The guluronate ring has the $^1C_4$(L) conformation. Sodium binds two translation-equivalent guluronate units and one water molecule in a primary five-fold coordination. The complexing oxygen functions, which include all axial hydroxyl groups and one carboxylate oxygen atom in the guluronate ring, describe a distorted trigonal bipyramid. A prominent feature of the crystal structure is the stacks of sodium atoms and guluronate residues in alternating sequence along the *c* axis. The stacks are held together by an intricate system of hydrogen bonds involving all oxygen atoms in the structure. The water molecules play an important role in this system both as hydrogen donors and acceptors.

INTRODUCTION

α-L-Guluronic acid is one of the two uronic acid constituents of the linear copolymer alginate, which is found primarily in brown algae as a mixed Na-Mg-Ca-Sr salt. The physical properties of alginate, in particular its mechanical strength and flexibility, are intimately related to the monomer composition and sequence in the polymer, and to the valency and coordination properties of the counterion[1,2]. Models of the chain stacking and intra- and inter-chain bonding have been proposed from a variety of physico-chemical measurements[1], including X-ray fibre diffraction studies of the poly-α-L-guluronic and poly-β-D-mannuronic acids[3–5]. Single-crystal structure data for the monomers or their salts seem to be lacking, probably because they are difficult to crystallise. We now report on a structure study of sodium α-L-guluronate dihydrate.

0008-6215/85/$ 03.30

EXPERIMENTAL

The preparation of crystalline sodium α-L-guluronate dihydrate (**1**) has been described[6,7].

Cell dimensions were determined from the setting angles of 18 reflections with $30° < 2\theta < 40°$ (Table I). Measurements made both before and after data collection showed the variation in all parameters to be within 2σ. Intensities of the equivalent reflection classes *h k-l* and *-h-k-l*, a total of 3415 excluding extinctions, were measured without attenuators to a maximum $(\sin\theta)/\lambda = 0.704$ Å^{-1} with Nb-filtered MoKα radiation on a Picker FACS-1 diffractometer controlled by the Vanderbilt disk-oriented program system[8]. Scan mode, $\omega/2\theta$; scan rate, 2°/min; basic scan range, $2\theta(\bar{\alpha}) - 0.9°$ to $2\theta(\bar{\alpha}) + 1.15°$; background measured 20 s at each end of the scan. Separate measurements of reflections with $2\theta < 13.5°$ were made with reduced low-angle scans to avoid or minimise the effect of the Nb K absorption edge. Three standard reflections were monitored at intervals of 70 reflections. The data were scaled according to the normalised, average standard curve, and routinely corrected for absorption and coincidence loss. These corrections are small in the present case, because of the low absorbance of the crystal (*cf.* Table I) and generally weak intensities (only one reflection had a count rate exceeding 10,000 c.p.s.). The Lorentz and polarisation corrections were applied. Six reflections were corrected for superposition in the scan range or background by the β-peak of a higher-order reflection; eight reflections at low 2θ angles were deleted because the Nb K edge was in the peak itself. Two partial data sets comprising 1637 pairs of corrected F^2 were weight-averaged and another 36 single measurements added to give a set of 1673 unique F^2. Weights and standard deviations were calculated according to expressions given previously[9]. The parameter S in the relation $\sigma^2(I) = \sigma^2_{count} + (SI_{net})^2$ was determined as 0.026. The internal consistency index $D = \Sigma|F_1^2 - F_2^2|/F^2_{av}$ for 1637 reflection pairs was 0.062. This relatively high value must be viewed in relation to the large proportion of weak intensities in the data. Of the reflections, 86 had $F^2 \leq \sigma(F^2)$ and were given zero weight.

TABLE I

CRYSTAL DATA FOR SODIUM α-L-GULURONATE DIHYDRATE (**1**)

Composition	$C_6H_{13}O_9Na$	λ(Å)	0.71073
Mol. wt.	252.15	Z	4
$F(000)$	528	D_x (Mg.m^{-3})	1 708(1)
Space group	$P2_12_12_1$	τ'^a (counts^{-1})	4.5×10^{-8}
a(Å)	7.591(2)	μ (mm^{-1})	0 187[b]
b	18.884(5)	Abs. corr. range	1.015–1 023
c	6.842(2)	Size (mm^3)	~0 38 × 0.15 × 0.12
V(Å^3)	980.8(5)	$[\alpha]_D^{23}$ (degrees)	+48 (*c* 2, water)
T(K)	87		

[a] τ' is the coincidence loss constant. [b] Mass absorption coefficients taken from ref. 39.

The structure was solved by direct methods, using a local Σ_2 multisolution tangent-refinement program[10]. The E map for the best phase model showed all non-hydrogen atoms except oxygen in one of the water molecules. This oxygen and all hydrogen atoms were located in a ΔF map following isotropic refinement of the known partial structure.

At the position of the hydrogen atom bonded to C-1, there appeared a diffuse and strong peak of maximum density ~1.6 eÅ^{-3}, about twice as dense as the other hydrogen peaks. These features and the long distance (~1.2 Å) from C-1 suggested that a small amount of the β anomer is present in the crystal. A very similar situation was encountered with α-di-*N*-acetylchitobiose monohydrate[11], and several other examples of anomeric disorder in crystalline carbohydrates have been reported[11]. Consequently, in addition to the hydrogen atom, an equatorial oxygen O-1β, with site occupancy 0.20, was placed 1.4 Å away from C-1, and population parameters for both O-1α and β were refined independently, together with the other variables. The coordinates of H-C1 and O-1β had to be constrained during the refinement; final distances from C-1 were 0.95 and 1.35 Å, respectively. The refined values of the population parameters were 0.92(1) for O-1 and 0.10(1) for O-1β, indicating that ~10% of the β anomer was present in the crystal.

Refinement was by full-matrix least squares, minimising the quantity $\Sigma w(|F_o| - k|F_c|)^2$ with weights $w = 1/\sigma^2(F_o)$. Hydrogen atoms and O-1β were refined isotropically and other non-hydrogen atoms anisotropically, and a correction for anomalous scattering was applied to Na. A summary of the refinement indicators is given in Table II.

The residual density in the final difference map ranges from −0.28 to 0.40 eÅ^{-3}, including maxima of density 0.28–0.40 eÅ^{-3} in all C–C bonds. The Na atom resides on positive density ~0.2 eÅ^{-3}, and there are maxima and minima of magnitude 0.25 eÅ^{-3} in the vicinity of this atom. Both water oxygen atoms are located on positive density ~0.2 eÅ^{-3}; the hydrogen atoms H-W12 and H-W21 are on or close to peaks 0.25–0.3 eÅ^{-3}. Near both water molecules, there are other residual maxima in the same density range, which could indicate partial disorder related to the presence of a small proportion of the β anomer. Several attempts were made to assign hydrogen atoms with partial occupancy to some of these

TABLE II

REFINEMENT PARAMETERS

$(\sin\theta)/\lambda$ range (Å^{-1})	0–0.704
Number of reflections with $w \neq 0$, NO	1587
Number of reflections with $w = 0$	86
Number of variables, NV	197
$R(F) = \Sigma\|\|F_o\| - k\|F_c\|\|/\Sigma\|F_o\|$	0.043
$R_w(F) = [\Sigma w(\|F_o\| - k\|F_c\|)^2/\Sigma wF_o^2]^{1/2}$	0.033
$GOF = [\Sigma w(\|F_o\| - k\|F_c\|)^2/(NO - NV)]^{1/2}$	1.65
Maximum shift/error, last cycle	0.006

positions in order to include possible alternate orientations of the water molecules, but without definite improvement. The final description of the water structure, therefore, is probably incomplete and does not provide additional information on the question of anomeric disorder. The final atomic parameters are given in Table III*.

Atomic scattering factors were those of Doyle and Turner[1] except for hydrogen[13]. A set of local programs was used for analyses and reduction of the data[14]; calculations following the structure solution were made with XRAY-76[15] crystallographic programs. Drawings of molecules were made by ORTEP[16].

RESULTS AND DISCUSSION

Molecular conformation. — Fig. 1 shows the structure of **1** with the atomic numbering. The conformation is $^1C_4$, and the puckering parameters[17,18] are: Q = 0.571 Å, θ = 174.2°, ϕ = 139.3°. The torsion angles are given in Table IV. The flattening of the ring in the region C-1 to C-4 is a consequence of the repulsion between axially oriented atoms or groups, O-1 · · · O-3 and O-4 · · · H-C2. Very similar distortions have been found in several D-*glycero*-D-*gulo*-heptopyranose rings[19]. The carboxyl group is only ~14° from being coplanar with O-5–C-5–C-6, and C-5, C-6, O-6, and O-7 are coplanar at the 5% significance level (χ^2 = 3.7).

Bond lengths and angles. — These parameters are shown in Table V. Bond lengths in the hemiacetal moiety C-5–O-5–C-1–O-1 are near the average values for α-pyranoses[20] (in brackets): 1.441 (1.443)–1.429 (1.426)–1.390 (1.398). The parent bond angles at O-5 and C-1, 112.8 (113.7) and 112.3° (111.7°) are more equal in **1** than in the average α-pyranose. Excluding O-5–C-1 and C-1–O-1, the lengths of all endo- and exo-cyclic C–C and C–O bonds involving the ring atoms are in good agreement with the corresponding values for methyl D-*glycero*-α-D-*gulo*-heptopyranoside calcium chloride hydrate[21]. The average and maximum differences between the two structures are 0.0035 and 0.011 Å, respectively. The lengths of the two C–O bonds in the carboxyl group are equal [1.262(3)], indicating a delocalisation of the charge. The refined H–O–H bond angles of the water molecules are 95(4) at O-W1 and 118(4)° at O-W2, the latter value lying well outside the normal range for the type of coordination in which O-W2 is involved[22]. The significance of these results is questionable, however, since the hydrogen parameters probably are affected by the residual density in this region.

The sodium coordination. — The sodium atom is surrounded by seven oxygen atoms as shown in Fig. 1. Two Na–O contacts, Na–O-5 [2.725(2) Å] and Na–O-2^{IV}** [2.849(2) Å], are distinctly longer than the other five which are in the range 2.344(2)

*Tables of anisotropic thermal parameters for the non-hydrogen atoms and observed and calculated structure factors have been 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/321/*Carbohydr Res.*, 145 (1985) 13–24.

** The superscript ^{IV} denotes the molecule at x, y, 1 + z The symmetry code is explained in Table VI.

TABLE III

FINAL ATOMIC PARAMETERS FOR SODIUM α-L-GULURONATE DIHYDRATE (**1**) AT 87 K. E S D 'S ARE GIVEN IN PARENTHESES

Atom	*Fractional coordinates*[a]				*Atom*	*Fractional coordinates*[a]			
	x	*y*	*z*	U_{eq}[b]		*x*	*y*	*z*	U_{iso}[c]
Na	3297(1)	1246(1)	7635(1)	126(4)	O-1β	525	36	269	16(6)
C-1	3951(3)	830(1)	2334(3)	96(10)	H-C1	498	56	261	−1(6)
C-2	4666(3)	1583(1)	2125(3)	83(10)	H-C2	525(3)	169(1)	335(4)	2(6)
C-3	3232(3)	2137(1)	1900(3)	89(9)	H-C3	381(3)	261(1)	205(3)	4(6)
C-4	1848(3)	2043(1)	3525(3)	80(9)	H-C4	83(3)	237(1)	326(3)	1(6)
C-5	1222(3)	1277(1)	3562(3)	78(10)	H-C5	66(3)	119(1)	231(3)	−6(5)
C-6	−93(3)	1158(1)	5213(3)	102(10)	H-O1	332(5)	13(2)	60(5)	46(10)
O-1	3247(3)	584(1)	586(3)	127(9)	H-O2	652(4)	140(2)	52(5)	25(9)
O-2	5830(2)	1648(1)	498(3)	127(8)	H-O3	188(4)	243(2)	−18(5)	20(7)
O-3	2413(2)	2058(1)	33(2)	118(7)	H-O4	290(4)	258(2)	540(5)	27(9)
O-4	2570(2)	2194(1)	5411(2)	98(7)	H-W11	674(5)	88(2)	631(5)	43(10)
O-5	2700(2)	813(1)	3894(2)	84(7)	H-W12	643(6)	55(2)	791(16)	56(12)
O-6	−1612(2)	1415(1)	4960(3)	125(7)	H-W21	601(6)	−76(2)	413(6)	55(12)
O-7	415(2)	824(1)	6703(2)	135(8)	H-W22	645(5)	−27(2)	562(6)	50(11)
O-W1	5903(2)	611(1)	6814(3)	137(8)					
O-W2	6673(2)	−651(1)	4939(3)	159(8)					

[a]Fractional coordinates × 10^4 for non-hydrogen atoms excluding O-1β; × 10^3 for hydrogen atoms and O-1β. [b]U_{eq}(Å^2 × 10^4) calculated from $U_{eq} = {}^1/_3 \Sigma_{ij} U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$ where U_{ij} are defined by $T(\theta) = \exp[-2\pi^2(U_{11}a^{*2}h^2 + \cdots + 2\,U_{12}a^*b^*hk + \cdots)]$. [c]$U_{iso}$ (Å^2 × 10^3) is defined by $T(\theta) = \exp[-8\pi^2U^2(\sin\theta)^2/\lambda^2]$.

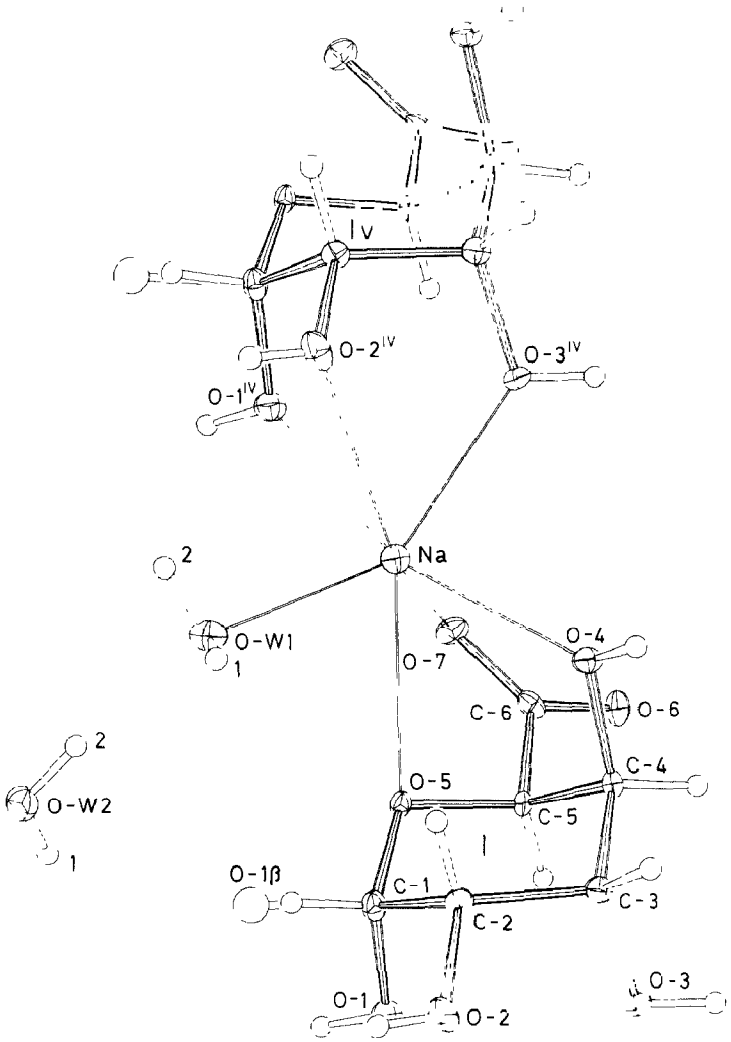

Fig. 1 Molecular conformation and atomic notation of sodium α-L-guluronate dihydrate (**1**). The guluronate unit at x, y, 1 + z (IV) has been included to show the environment of the sodium atom. Thermal ellipsoids correspond to a 50% probability.

–2.414(2) Å. Therefore, we prefer to describe the coordination as five-fold, each Na linking one water molecule O-W1 and two L-guluronate rings, of which one chelates Na through O-7 in the carboxyl group and the axial HO-4, and the second through the axial HO-1 and HO-3. The five oxygen atoms form a distorted trigonal bipyramid (Fig. 2), a geometry observed in other five-coordinated Na complexes[23,24]. The axial angle O-4–Na–O-1^{IV} is 157.34(7)°, and the equatorial angles O-3^{IV}–Na–O-W1, O–W1–Na–O-7, and O-7–Na–O-3^{IV} are 137.10(7), 121.65(7), and 98.14(7)°, respectively. The mean Na–O distance, 2.385 Å, is near the expected[25] value, 2.40 Å.

TABLE IV

ENDO- AND EXO-CYCLIC TORSION ANGLES (°)[a]

O-5–C-1–C-2–C-3	−53.6	O-1–C-1–C-2–O-2	−51.2
C-1–C-2–C-3–C-4	50.5	O-2–C-2–C-3–O-3	54.6
C-2–C-3–C-4–C-5	−52.1	O-3–C-3–C-4–O-4	−173.8
C-3–C-4–C-5–O-5	58.8	O-4–C-4–C-5–C-6	56.5
C-4–C-5–O-5–C-1	−64.7	C-5–O-5–C-1–O-1	−63.6
C-5–O-5–C-1–C-2	60.5	C-5–O-5–C-1–O-1β	−177.0
		C-4–C-5–C-6–O-7	−105.9
		O-5–C-5–C-6–O-7	14.0

[a]Signs of torsion angles follow the convention of Klyne and Prelog[40]; e.s.d.'s are in the range 0.15–0.25°.

TABLE V

BOND LENGTHS (Å) AND ANGLES (°)

Bonds			
C-1–C-2	1.531	C-1–O-1β	1.35
C-2–C-3	1.518	C-2–O-2	1.427
C-3–C-4	1.540	C-3–O-3	1.429
C-4–C-5	1.524	C-4–O-4	1.431
C-5–O-5	1.441	C-5–C-6	1.523
O-5–C-1	1.429	C-6–O-6	1.263
C-1–O-1	1.390	C-6–O-7	1.260
Angles			
O-5–C-1–C-2	109.0	C-1–C-2–O-2	111.9
C-1–C-2–C-3	113.3	C-3–C-2–O-2	107.8
C-2–C-3–C-4	109.7	C-2–C-3–O-3	109.3
C-3–C-4–C-5	109.6	C-4–C-3–O-3	109.7
C-4–C-5–O-5	109.7	C-3–C-4–O-4	111.5
C-5–O-5–C-1	112.8	C-5–C-4–O-4	107.0
		C-4–C-5–C-6	110.9
C-2–C-1–O-1	111.5	O-5–C-5–C-6	107.7
O-5–C-1–O-1	112.3	C-5–C-6–O-6	116.1
C-2–C-1–O-1β	111.7	C-5–C-6–O-7	118.2
O-5–C-1–O-1β	109.6	O-6–C-6–O-7	125.7

Bonds and angles involving H

Type	*Number*	*Range*	*Mean*	σ_{av}
C–H[b]	4	0.97–1.00	0.98	0.02
O–H	4	0.70–0.85	0.79	0.03
O–H (water)	4	0.78–0.88	0.85	0.04
X[c]–C–H[b]	12	106–112	109	1
C–O–H	4	106–113	108	2
H–O–H	2	95–118	106	4

[a]E.s.d.'s in bonds and angles involving non-hydrogen atoms excluding O-1β are 0.003 Å and 0.2°, respectively. [b]Excluding bond and angles involving H–C1. [c]X = C,O.

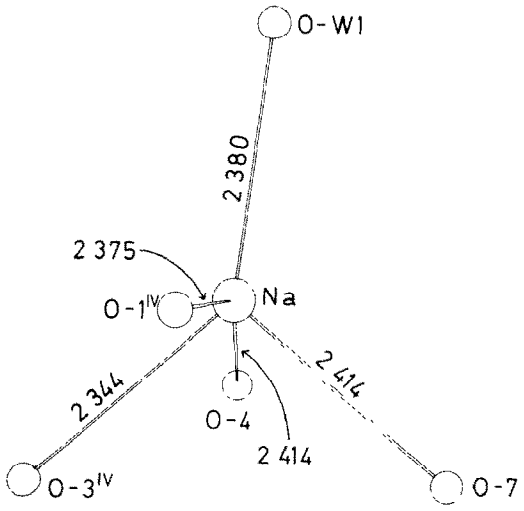

Fig. 2. The primary sodium coordination geometry. Angle values are given in the text. E s.d. in the bonds is 0.002 Å.

Several studies have been made of the interaction between various atoms and both neutral and anionic carbohydrates. Complexes with calcium have been investigated extensively both in solution and in the crystalline state[26–29]. The data clearly show that the Ca–hydroxyl contact is a major structural element, presumably needed to satisfy the topological requirements of the calcium atom for complex formation. According to Cook and Bugg[27], this is true even with carbohydrates possessing a formally anionic moiety, for example, a carboxylate group. It was observed by these authors[27] that anionic substituents may enhance the Ca-binding properties of carbohydrates, but they are not necessary for the formation of complexes in aqueous solution or in the solid state.

In **1**, the carboxyl group contributes to sodium binding, as would be expected from a simple electrostatic model. However, prediction of coordination sites in such complexes may be misleading because the distribution of charge in general is not known. Accurate studies of the electronic structure in other types of ionic compounds have provided relevant data. Thus, in the crystal structures of NaSCN[30] and NH_4SCN[31], the charge transfer from cation to anion was found to be considerably less than expected for a purely ionic model, ~0.25 and ~0.55 electron, respectively. In the structures of NaCN · 2 H_2O[32] and Na sulfanilate · 2 H_2O[33], the net charge on Na was only about +0.1 e or less, *i.e.*, nearly neutral; charges on the water molecules were in the range +0.15 to +0.25 e. These results emphasise that a straightforward assignment of charges in the **1** complex, with a positive unit charge on sodium and a negative unit charge on the carboxyl group, is likely to be incorrect. A more realistic model would be one in which the net atomic charges are smaller and more evenly distributed over the structure. Data for other crystalline hydrates[32,33] (*cf.* also Coppens *et al.*[34]) infer that there may be a significant ac-

cumulation of positive charge on the water molecules, the cation being partially or nearly neutralised.

There is also experimental evidence that carboxyl groups in charged ligands are not necessarily engaged in coordination with alkali or alkaline earth atoms; examples are: K(D-gluconate) · H_2O, crystal form A[35], Sr 4-*O*-(4-deoxy-β-L-*threo*-hex-4-enosyl)-α-D-galacturonate · 4.5 H_2O[36], Mg (+)-malate · 5 H_2O[37], and Mg bis(hydrogenmaleate) · 6 H_2O[38]. It is reasonable to assume, therefore, that the most important principle in complexes with sodium is also the spatial requirements of this atom for chelation. Consequently, the participation of a carboxyl oxygen in **1** relates primarily to its accessibility, rather than implying a preferred chelation site due to high negative charge.

The crystal structure. — Fig. 3 depicts the molecular packing. Hydrogen bonds are shown as dashed lines, and the sodium coordination polyhedra have been omitted for clarity. Geometric details of the hydrogen bonds are given in Table VI, where contact distances and angles involving hydrogen have been recalculated with H positions normalised to standard neutron-diffraction O–H bond-lengths[19].

Each sodium atom (hatched in Fig. 3) chelates two translation-equivalent guluronate units, thus creating stacks · · · GulA · · · Na · · · GulA · · · Na · · · related by symmetry along the *c* axis. The stacks are laced together by an extensive system of hydrogen bonds in which all oxygen atoms take part. All four hydroxyl groups in the guluronate ring are hydrogen donors, with O-1 in a weaker, bifurcated hydrogen-bond. Only the equatorial O-2 serves also as an acceptor; the

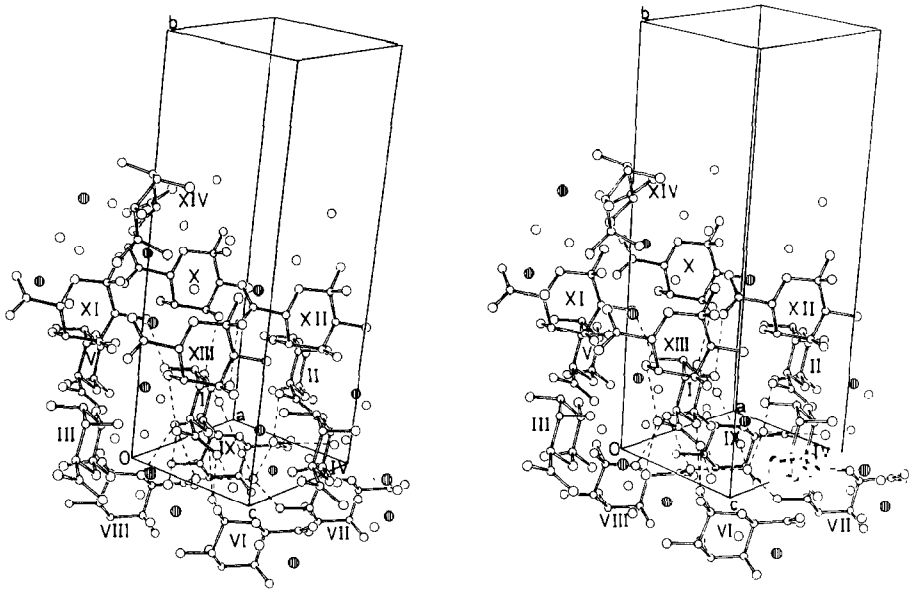

Fig 3. Stereodrawing of the molecular packing with hydrogen bonds drawn as broken lines. The sodium atoms are shown as hatched circles. Numbering of molecules corresponds to the symmetry code given in Table VI.

TABLE VI

GEOMETRY OF THE HYDROGEN-BONDING SYSTEM

Symmetry code

I	x	y	z	VIII	1/2 − x	−y	−1/2 + z
II	1 + x	y	z	IX	3/2 − x	−y	−1/2 + z
III	−1 + x	y	z	X	1/2 + x	1/2 − y	−z
IV	x	y	1 + z	XI	−1/2 + x	1/2 − y	−z
V	x	y	−1 + z	XII	1/2 + x	1/2 − y	1 − z
VI	1/2 − x	−y	1/2 + z	XIII	−1/2 + x	1/2 + y	1 − z
VII	3/2 − x	−y	1/2 + z	XIV	−x	1/2 + y	1/2 − z

Hydrogen bonds with e.s.d.'s in parentheses

D–H · · · A	*D · · · A* (Å)	*H · · · A* (Å)	$(H \cdots A)^a_{corr}$ (Å)	$\angle(DHA)^a_{corr}$ (°)
O-1–H · · · O-5^{VIII}	2 970(2)	2.27(4)	2.18	137
O-1–H · · · O-7^{VIII}	2.946(3)	2.18(4)	2.07	148
O-2–H · · · O-W2^{IX}	2.700(3)	2.01(3)	1.74	164
O-3–H · · · O-2^{XI}	2.747(2)	1.92(3)	1.77	173
O-4–H · · · O-6^{XII}	2 711(2)	1.94(3)	1.74	169
O-W1–H-1 · · · O-6^{II}	2.734(2)	1.86(4)	1.76	173
O-W1–H-2 · · · O-W2^{VII}	2.822(3)	2.01(4)	1.90	158
O-W2–H-1 · · · O-7^{VIII}	2.743(3)	1.98(4)	1.79	164
O-W2–H-2 · · · O-W1^{I}	2.769(3)	1.90(4)	1.79	173

Possible hydrogen bonds involving O-1β

O_1	O_2	$O_1 \cdots O_2$[b] (Å)	O_1	O_2	$O_1 \cdots O_2$[b] (Å)
O-1β	O-W1^{I}	2.89	O-1β	O-W2^{IX}	3.04
O-1β	O-W2^{I}	2.63	O-1β	O-7^{VIII}	2.37

[a]With O-H bond-lengths normalised to 0.98 Å[41]. [b]C-1–O-1β distance, 1.40 Å.

other hydroxyl oxygen atoms are involved in the primary sodium-coordination shell. Each carboxyl oxygen atom accepts two hydrogen bonds. The two water molecules contribute significantly to the cohesive forces in the crystal. O-W1 is twice donor, once acceptor, and participates in the sodium coordination; O-W2 is involved in four hydrogen bonds, twice as a donor and twice as an acceptor.

The accommodation of ~10% of the β anomer in the crystal implies a subsidiary pattern of hydrogen bonds; O-1β makes at least three contacts with other oxygen atoms within the range for hydrogen bonding. The distance to O-7^{VIII}, 2.37 Å (with C-1–O-1β fixed at 1.40 Å), corresponds to a very short and strong hydrogen bond in which O-1β must be the donor. In the possible hydrogen bond(s) to O-W2 (and O-W1) of the same asymmetric unit, O-1β presumably is the acceptor. The refined hydrogen positions, however, are not compatible with this scheme, which

would require a reorientation of the water molecule(s). The residual density in the water region indicates some kind of defect, due perhaps to partial, orientational disorder of the water molecules. The electron density corresponding to a hydrogen atom with site occupancy of ~10% would be in the range 0.05–0.1 $eÅ^{-3}$, which is below the noise level in the present study. Therefore, direct evidence of hydrogen atoms engaged only in bonding with O-1β cannot be obtained.

ACKNOWLEDGMENT

This work was supported in part by Grant D.22.52.005 from Norges Almenvitenskapelige Forskningsråd (NAVF).

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