Interactions of Cations with Sugar Anions. Part II.[1] Crystal Structure of Strontium 4-*O*-(4-Deoxy-β-L-*threo*-hex-4-enosyl)-α-D-galacturonate–4.5 Water

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The crystal structure has been determined for the title compound (1) from 1 928 visually estimated reflections. The structure was solved by the heavy-atom method and refined by block-diagonal least-squares to R 0.11. Two molecules of the disaccharide exist in each asymmetric unit and, since the space group is $P2_1$, each unit cell [a = 12.81(1), b = 11.29(1), c = 14.81(2) Å; β = 119.3(4)°] contains 4 disaccharide residues, 4 Sr ions, and 18 H_2O molecules. One of the unsaturated residues in the asymmetric unit adopts the $^2H_1$ half-chair conformation, whereas the other adopts the $^1H_2$, so that the glycosidic linkages in the two independent disaccharides are axial–axial and equatorial–axial respectively. The two independent strontium ions are co-ordinated similarly by three water molecules and the same five oxygen atoms of three saturated residues, in a distorted square antiprism. Unsaturated residues do not co-ordinate to Sr^{2+}, even though they carry a formal negative charge at the carboxylate.

The glycosidic bond angles are rather smaller than expected: 112 in the axial–axial and 115° in the equatorial–axial conformer. Glycosidic torsion angles in the axial–axial form adopt values close to those in our model for sodium pectate. Carboxylate and ring oxygens form bidentate arrangements which co-ordinate to Sr^{2+}.

In an earlier paper,[1] we outlined the occurrence of sugar carboxylate anions as residues in biopolymers and the importance of their interactions with divalent cations, especially Ca^{2+}. The simplest natural sequences of these residues are in pectins and alginates where [2] they exist in the consecutive sequences, poly-(D-galacturonate),

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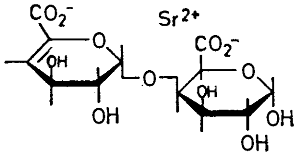
[1] Part I, S. E. B. Gould, R. O. Gould, D. A. Rees, and W. E. Scott, *J.C.S. Perkin II*, 1975, 237.

[2] G. O. Aspinall, ' Polysaccharides,' Pergamon, Oxford, 1970; D. A. Rees, *Adv. Carbohydrate Chem. Biochem.*, 1969, **24**, 369.

poly-(L-guluronate), and poly-(D-mannuronate). We hoped to gain some understanding of likely chain conformations and interactions with cations by study of the crystal structures of suitable fragments of these polymers: (i) those derived by acid or enzymic hydrolysis which are di- and oligo-saccharides of the familiar, saturated type, or (ii) those derived by a chain-splitting mechanism which involves β-elimination and is catalysed by base and by a second group of enzymes leading to products in which one residue is unsaturated. We have so far failed to obtain single crystals of relevant salts of the first type, but we now report the three-dimensional crystal structure of a salt of the second type, namely strontium 4-*O*-(4-deoxy-β-L-*threo*-hex-4-enosyl)-D-galacturonate (1). This compound had previously been isolated in microcrystalline condition from an enzymic hydrolysate of pectic acid.[3] It is of interest not only for the foregoing reasons, but also because it is the first crystal structure to be characterised in which a sugar ring is unsaturated between C(4) and C(5). We can compare the ring conformation of this residue in the solid state with evidence for those of related compounds in solution.[4-6]



(1)

TABLE 1

Positional * and thermal parameters (all × 10^4), showing the corresponding atoms of the two independent molecules in adjacent columns

Atom	*x*	*y*	*z*	*U*	Atom	*x*	*z*	*y*	*U*
Sr(1)	1 319	2 409	1 642	†	Sr(2)	−3 930	2 540	1 458	†
C(1)	496	5 251	233	185	C(21)	−4 269	5 352	269	230
C(2)	873	6 454	825	301	C(22)	−3 775	6 331	1 071	224
C(3)	2 049	6 868	911	316	C(23)	−2 602	6 797	1 182	249
C(4)	3 054	5 996	1 223	194	C(24)	−1 703	5 839	1 537	97
C(5)	2 476	4 820	627	96	C(25)	−2 252	4 719	852	83
C(6)	3 396	3 748	1 086	245	C(26)	−1 442	3 619	1 403	193
O(1)	191	5 598	−825	213	O(21)	−4 399	5 708	−666	187
O(2)	−80	7 287	355	261	O(22)	−4 740	7 322	588	318
O(3)	2 444	7 920	1 534	424	O(23)	−2 209	7 809	1 814	328
O(4)	3 514	5 752	2 313	171	O(24)	−1 366	5 547	2 606	242
O(5)	1 426	4 364	640	176	O(25)	−3 405	4 377	728	178
O(6)	3 081	2 938	1 449	437	O(26)	−1 860	2 644	1 620	345
O(7)	4 341	3 878	1 070	252	O(27)	−394	3 632	1 530	221
C(11)	4 752	5 628	2 842	99	C(31)	−109	5 539	3 306	263
C(12)	5 332	5 452	4 020	439	C(32)	40	4 968	4 272	409
C(13)	4 799	6 376	4 401	272	C(33)	1 434	5 044	5 119	289
C(14)	4 953	7 648	4 068	269	C(34)	2 022	6 198	5 092	559
C(15)	5 113	7 791	3 242	233	C(35)	1 486	6 854	4 277	340
C(16)	5 141	8 922	2 788	161	C(36)	2 054	8 070	4 252	380
O(12)	4 880	4 307	4 103	252	O(32)	−530	5 697	4 664	471
O(13)	5 512	6 357	5 549	367	O(33)	1 984	4 010	4 895	573
O(15)	5 299	6 793	2 727	245	O(35)	331	6 759	3 441	433
O(16)	5 376	8 914	2 032	329	O(36)	2 880	8 401	5 126	578
O(17)	5 104	9 820	3 224	596	O(37)	1 788	8 528	3 370	652
O(51)	2 465	3 749	3 217	408	O(56)	−2 881	3 907	3 008	336
O(59)	1 938	951	3 262	410	O(55)	−4 607	1 939	2 759	378
O(52)	2 450	589	1 462	463	O(54)	−2 892	532	1 812	579
O(53)	9 604	1 130	3 177	787	O(57)	−2 107	7 410	3 695	678
O(58)	−214	8 620	1 746	395					

* Mean errors of positional parameters × 10^4

	σ_x	σ_y	σ_z
Sr	2	4	2
C	23	34	20
O(sugar)	18	26	16
O(H_2O)	23	31	20

† Anisotropic thermal parameters

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sr (1)	200	333	240	−26	89	−34
Sr (2)	177	259	220	−30	85	17

Thermal parameters are in the form: isotropic, $\exp(-8\pi^2 U \sin^2\theta/\lambda^2)$; anisotropic, $\exp(-2\pi^2 \Sigma h_j a_i^* h_j a_j^* U_{ij})$.

EXPERIMENTAL

Preparation and Analysis.—The microcrystalline material [3] was dissolved in water, filtered, and the filtrate and washings heated to 80 °C. Redistilled isopropyl alcohol was added to incipient turbidity, keeping the mixture at 70—80 °C throughout. The solution was then seeded, stoppered, and left in a thermostat at 38 °C. After several days, crystals were filtered off, washed with aqueous isopropyl alcohol, and air-dried. Recrystallisation was repeated in the same way (Found: C, 27.8; H, 4.35.

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[3] S. Hasegawa and C. W. Nagel, *J. Biol. Chem.*, 1962, **237**, 619.

[4] J. Kiss and F. Burkhardt, *Helv. Chim. Acta*, 1970, **53**, 1000.

[5] D. M. Mackie and A. S. Perlin, *Carbohydrate Res.*, 1972, **24**, 67.

[6] A. S. Perlin, D. M. Mackie, and C. P. Dietrich, *Carbohydrate Res.*, 1971, **18**, 185.

$C_{12}H_{14}O_{12}Sr,4\frac{1}{2}H_2O$ requires C, 27.8; H, 4.45%). The formula was confirmed by the structure determination.

Crystal Data.—$C_{24}H_{46}O_{33}Sr_2$, Monoclinic. M = 1 037, a = 12.81, b = 11.29, c = 14.81 Å, β = 119.3°, U = 1 868 Å^3, D_c = 1.83, Z = 2, D_m = 1.84 g cm^{-3}. Cu-K_α = 1.5418 Å, μ(Cu-K_α), 52 cm^{-1}. Space group $P2_1$, from systematic absences and optical activity.

Data Collection and Solution of the Structure.—Weissenberg photographs were taken for layers $h0$—$5l$ and 0—$1kl$. Intensities were estimated visually and put on a common scale by use of common reflections. Absorption corrections were not made. The best crystals were irregular plates, thickness 0.05 mm, and exposures of up to 120 h were required. After two such exposures, some crystals showed marked signs of deterioration. In all 1928 independent intensities were estimated as being significantly above background.

The most striking feature of the data is the relative weakness of spots with odd values of h. In terms of the mean value of the squares of the normalised structure factors, this may be summarised by: $E^2(2n, k, l,)/E^2(2n + 1, k, l)$ = 1.97. The three-dimensional Patterson function could be easily interpreted in terms of there being two pairs of crystallographically independent strontium ions, related by a pseudo-repeat at $x = \frac{1}{2}$. Two equally possible solutions to the Patterson have $x_1 = 0.371$, $x_2 = 0.871$ and $x_1 = 0.121$, $x_2 = 0.621$. In both cases $z_1 = z_2 = 0.154$ and $y_1 = y_2 = y$ which may be fixed arbitrarily to define the origin; the other two strontium ions in the cell are related to these by the screw axes. Both solutions represent the same array of atoms; in either case the symmetry elements are equivalent to the pseudosymmetry elements of the other. Structure factors were calculated based on both arrays, taking $y = 0.25$, and both gave R 0.49 based on all reflections. In both structures, the atoms were then moved off positions of pseudosymmetry to different grid positions, and finally refined by least squares. In the best positions, contribution to reflections with $h = 2n + 1$ was significant, and R for set 1 and set 2 positions was 0.39 and 0.32. Electron-density maps phased by the strontium atoms in essentially their final positions showed the two independent reducing residues quite clearly in positions also almost related by a pseudo-repeat. All these atoms as well as C(11) and C(31) in the nonreducing residues were included in a structure-factor calculation which give R 0.28 and a difference map almost free of pseudosymmetry. One nonreducing residue and four of the water molecules were located in this map, and all non-hydrogen atoms were located in a further two cycles of structure factor and difference-Fourier calculations.

Refinement was by block-diagonal and large-block approximations because of computer size limitations. In early stages, all parameters of atoms related by the pseudo-repeat were refined in the same block. Unit weights were used for $|F_o| < A$, and a weight of $(A/F_0)^2$ was used otherwise, where $A = 50$. Anisotropic temperature factors were used for strontium only, and individual isotropic parameters for other atoms. The least squares converged at R 0.11. The final difference map showed several peaks with a density $\leqslant 0.5$ eÅ^{-3}, but these could not be related to meaningful hydrogen atom positions, and these were not detetermined. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21533 (5 pp., 1 microfiche).*

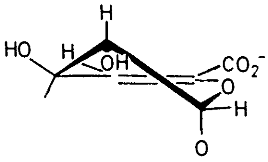
All standard calculations were performed at the Edinburgh Regional Computing Centre by use of the 1970 revision of the '*X*-Ray' program system.[7] Scattering factors were taken from ref. 8. Positional and thermal parameters are given in Table 1.

Numbering of Atoms.—We used the following convention:

C(1)—(6) O(1)—(7)	Atoms in the saturated residues of the disaccharide having axial–axial glycosidic linkage (see later)
C(11)—(16) O(12)—(17)	Atoms in the unsaturated residue of this disaccharide. It has the $^2H_1$ half-chair conformation
C(21)—(26) O(21)—(27)	Atoms in the saturated residue of the disaccharide having equatorial–axial glycosidic linkage (see later)
C(31)—(36) O(32)—(37)	Atoms in the unsaturated residue of this disaccharide. It has the $^1H_2$ half-chair conformation

For each atom, the last digit corresponds to the conventional numbering system for a single molecule, *e.g.* O(33) is an O(3), C(5) is a C(5'). O(51)—(59) are the oxygen atoms of water molecules

Description of the Structure.—The striking feature of this crystal structure is that the asymmetric unit consists of two disaccharide molecules which are configurationally identical but conformationally very different. In one, the unsaturated residue adopts the $^2H_1$ half-chair conformation [formula (2)] and the glycosidic linkage is axial–axial (3); in the other the corresponding stereochemistry is $^1H_2$ (4) and equatorial–axial (5). The two strontium ions differ in their co-ordination geometry, but only in minor ways (see later). As expected, the two saturated sugar rings exist in the Reeves C(1) chair conformation [$^4C_1$(D)]. These residues



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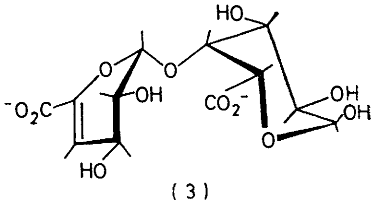

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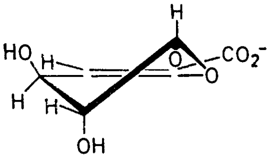

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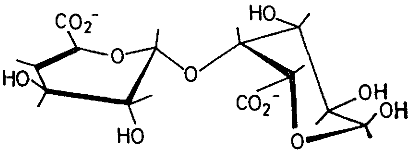

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

[7] '*X*-Ray' System,' Computer Science Centre, University of Maryland, Report TR 6758, version of 1970.

[8] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

TABLE 2

Summary of bond lengths (Å), bond angles (°), and absolute values of in-ring torsion angles (°)

	No. of values	Mean	σ of mean
(*a*) Bonds			
C–C	18	1.534	0.010
C=C	2	1.318	0.027
C–O	22	1.448	0.010
C=O	8	1.263	0.014
(*b*) Angles			
R–C–R (sp^3)	48	109.1	0.6
R–C–R (sp^2)	20	119.7	1.2
R–O–R	6	112.0	0.9
(*c*) Torsion angles			
R–C–C–R	10	51	2
R–C=C–R	2	9	2
R–C–C=R	4	23	2
R–C–O–R	8	59	3

have the α-configuration as in the related salts of galacturonic acid monomer.[1] Figure 1 shows the structure is shown projected on the 010 plane. Mean bond lengths and bond angles are shown in Table 2. The hydrogen bonding cannot be unambiguously assigned. Possible contacts are summarised in Table 3.

The Sr ··· O co-ordination distances (Table 4) are in the range 2.48—2.79 Å, with most values 2.50—2.60 Å. Both strontium ions have eight-fold co-ordination; each involves three water molecules and the same five oxygen atoms of the saturated residues of three disaccharide molecules, namely O(1) and O(2) from one residue, O(5) and O(6) from a second, and O(7) only from a third. The oxygen atoms of the unsaturated sugar residues are not co-ordinated to Sr^{2+}. The two co-ordination patterns are irregular and could be described as very distorted square antiprisms. They resemble each other closely except for the position of one water molecule (Figures 2 and 3).

DISCUSSION

Conformation of the Sugar Rings.—The existence of the unsaturated sugar residue in two distinctly different half-chair forms (2) and (4) in the same unit cell, is taken to indicate that the energies of these forms are nearly balanced so that the final state is determined by packing forces. Conformational analysis confirms that

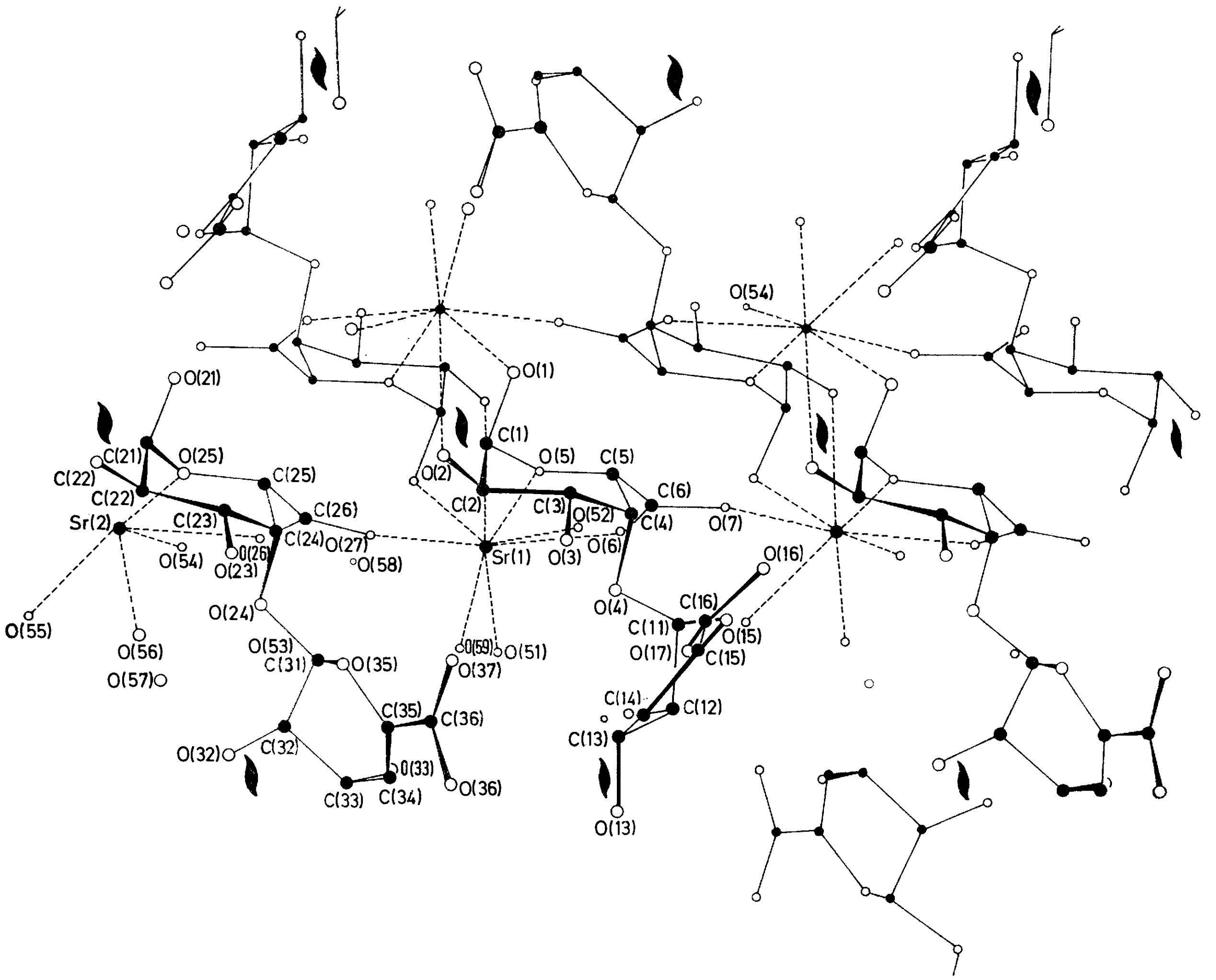

FIGURE 1 Projection of the structure of (1) on the 010 plane. Co-ordination of the cation is indicated by dashed lines. The origin of the unit cell is on the symmetry axis shown between O(2) and C(1), with O_x pointing towards the corresponding axis in the region of O(7) and O(54) and O_z pointing towards the corresponding axis near O(32)

similar sets of interactions exist within each, except for the following. (*a*) The $^2H_1$ form is disfavoured by one extra O ··· O gauche interaction. The corresponding energy difference should be somewhat less than the value [9] (1.6 kJ mol^{-1}) for saturated sugar rings because of the distortion from true equatorial geometry. (*b*) The $^2H_1$ form is disfavoured by the allylic effect,[10] according to which large groups at allylic positions show inverted stereochemical requirements. The magnitude of this effect is not known for the unsubstituted sugars but can be 3—5 kJ mol^{-1} for certain derivatives. (*c*) The $^2H_1$ form is favoured by the anomeric effect which, by analogy with saturated sugar rings,[9] could contribute a free-energy difference of *ca.* 3—4 kJ mol^{-1}. This value might be greater for our type of unsaturated ring because of the absence of an unfavourable interaction between O(1) and H(5).[5]

TABLE 3

Possible hydrogen bonds. Distances $\leqslant$3.25 Å are given for all pairs of oxygen atoms. Symmetry operations are defined in the footnote.

O(1) ··· O(58^{12})	2.6	O(52^{10})	3.0								
O(2) ··· O(58)	2.6	O(5^{10})	2.9								
O(3) ··· O(52^{3})	3.0										
O(4) ··· O(51)	3.2										
O(5) ··· O(2^{12})	2.9	O(58^{12})	3.2								
O(6) ··· O(52)	2.8	O(55^{2})	2.9	O(51)	3.2						
O(7) ··· O(55^{2})	3.1										
O(12) ··· O(36^{8})	2.7	O(51)	2.8								
O(13) ··· O(59^{7})	2.9	O(17^{8})	2.9								
O(15) ··· O(57^{2})	3.0	O(22^{2})	3.2								
O(16) ··· O(22^{2})	2.7	O(21^{10})	2.7	O(54^{1})	3.0						
O(17) ··· O(55^{1})	2.6	O(13^{7})	2.9	O(52^{3})	3.2						
O(21) ··· O(16^{12})	2.7	O(54^{13})	3.0	O(55^{13})	3.0	O(52^{10})	3.2				
O(22) ··· O(16^{5})	2.7	O(15^{5})	3.2	O(25^{13})	3.2						
O(23) ··· O(58)	2.8	O(57)	2.8	O(54^{3})	3.2	O(35)	3.2				
O(24) ··· O(56)	2.9	O(57)	3.1								
O(25) ··· O(56)	3.1	O(7^{5})	3.2	O(22^{14})	3.2						
O(26) ··· O(53^{5})	2.7	O(54)	2.8								
O(32) ··· O(57)	2.7	O(53^{7})	2.9								
O(33) ··· O(57^{11})	2.7	O(51)	2.9								
O(35) ··· O(58)	3.1	O(23)	3.2								
O(36) ··· O(12^{7})	2.7	O(56^{9})	2.8								
O(37) ··· O(48)	2.5	O(59^{3})	2.8								
O(51) ··· O(12)	2.8	O(33)	2.9	O(6)	3.2	O(59)	3.2	O(4)	3.2		
O(52) ··· O(6)	2.8	O(1^{12})	3.0	O(3^{4})	3.0	O(59)	3.1	O(17^{4})	3.2	O(21^{12})	3.2
O(53) ··· O(26^{2})	2.7	O(54^{2})	2.9	O(59^{2})	2.9	O(32^{8})	2.9				
O(54) ··· O(26)	2.8	O(53^{5})	2.9	O(16^{6})	3.0	O(21^{14})	3.0	O(23^{4})	3.2		
O(55) ··· O(17^{6})	2.6	O(6^{5})	2.9	O(21^{14})	3.0	O(56)	3.0	O(7^{5})	3.1		
O(56) ··· O(36^{11})	2.8	O(24)	2.9	O(55)	3.0	O(25)	3.1				
O(57) ··· O(33^{9})	2.7	O(32)	2.7	O(23)	2.8	O(15^{5})	3.0	O(24)	3.1		
O(58) ··· O(37)	2.5	O(2)	2.6	O(1^{10})	2.6	O(23)	2.8	O(35)	3.1	O(5^{10})	3.2
O(59) ··· O(37^{4})	2.8	O(53^{5})	2.9	O(13^{8})	2.9	O(52)	3.1	O(51)	3.2		

Superior numerals define the following symmetry operations:

1 $1 + x, 1 + y, z$
2 $1 + x, y, z$
3 $x, 1 + y, z$
4 $x, -1 + y, z$
5 $-1 + x, y, z$
6 $-1 + x, -1 + y, z$
7 $1 - x, \frac{1}{2} + y, 1 - z$
8 $1 - x, -\frac{1}{2} + y, 1 - z$
9 $-x, \frac{1}{2} + y, 1 - z$
10 $-x, \frac{1}{2} + y, -z$
11 $-x, -\frac{1}{2} + y, 1 - z$
12 $-x, -\frac{1}{2} + y, -z$
13 $-1 - x, \frac{1}{2} + y, -z$
14 $-1 - x, -\frac{1}{2} + y, -z$

The experimental evidence (n.m.r.) for analogous glycosides in $CDCl_3$[4] and in water [5] and for (1) and its homologues in aqueous solution,[6] would suggest that the outcome is actually in favour of the $^2H_1$ form and therefore that the anomeric effect is the dominant contribution.[5] The energy advantage is expected to be small, however, as indeed our results would indicate.

TABLE 4

Co-ordination of the strontium ions. Distances in Å, symmetry operations defined in footnote to Table 3

Sr(1)–O(5)	2.70	Sr(2)–O(25)	2.58
Sr(1)–O(6)	2.48	Sr(2)–O(26)	2.55
Sr(1)–O(27)	2.53	Sr(2)–O(7^{5})	2.50
Sr(1)–O(1^{12})	2.66	Sr(2)–O(21^{14})	2.79
Sr(1)–O(2^{12})	2.59	Sr(2)–O(22^{14})	2.66
Sr(1)–O(51)	2.56	Sr(2)–O(56)	2.54
Sr(1)–O(52)	2.60	Sr(2)–O(54)	2.55
Sr(1)–O(59)	2.69	Sr(2)–O(55)	2.56

Geometry at the Glycosidic Bridge.—Until recently, most crystal-structure determinations for disaccharide derivatives in which the residues are joined through two secondary position, have shown a narrow distribution of values for the glycosidic bond angles, in the range 116.5 ± 1° (for a review, see ref. 11). However, the crystal structures of (α,α-trehalose)$CaBr_2$ monohydrate (113.2°) [12] and *O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-(1 → 2)-*O*-β-D-xylopyranosyl-(1 → 4)-D-xylopyranose trihydrate (113.8 and 116.0°) [13] show that lower values can some-

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[9] S. J. Angyal, *Austral. J. Chem.*, 1968, **21**, 2737.

[10] R. J. Ferrier and G. H. Sankey, *J. Chem. Soc.* (*C*), 1966, 2345; R. F. Ferrier, *Adv. Carbohydrate Chem.*, 1969, **24**, 199.

[11] S. Arnott and W. E. Scott, *J.C.S. Perkin II*, 1962, 324.

[12] W. J. Cook and C. E. Bugg, *Carbohydrate Res.*, 1973, **31**, 265.

[13] R. A. Moran and G. F. Richards, *Carbohydrate Res.*, 1972, **25**, 270.

times exist. The glycosidic bond angles in both disaccharide residues in our asymmetric unit are in the lower range of values, namely 112° for the axial–axial and 115° for the equatorial–axial disaccharide.

No inter-residue hydrogen bonds are apparent in either of our disaccharides, except possibly between O(5) and O(3) in the equatorial–axial structure, although, even here, the O · · · O distance (3.18 Å) is very long. If the orientation of the carboxylate group were altered in the axial–axial dimer, an O(2) · · · O(6′) inter-residue hydrogen bond might be possible, similar to that in the poly-(L-guluronic acid) structure.[14] In our crystal structure, this group prefers to adopt an orientation in which it can co-ordinate two adjacent strontium ions.

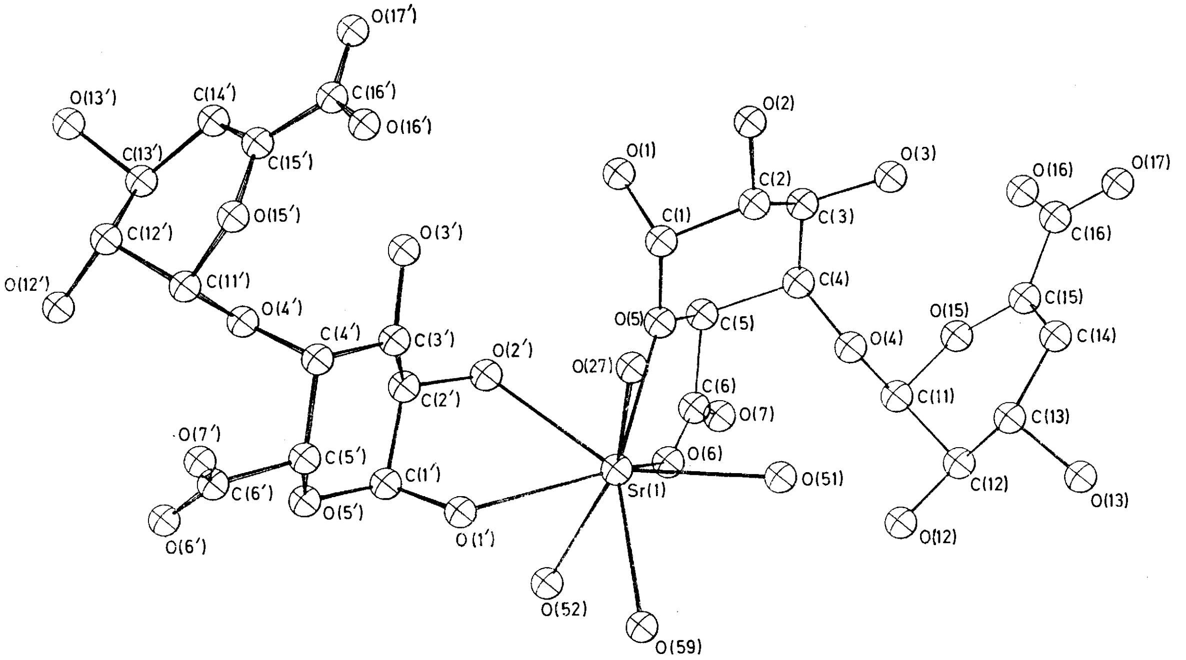

FIGURE 2 Cation co-ordination by the axial–axial disaccharide; primed atoms are at $-x, -\frac{1}{2}+y, -z$

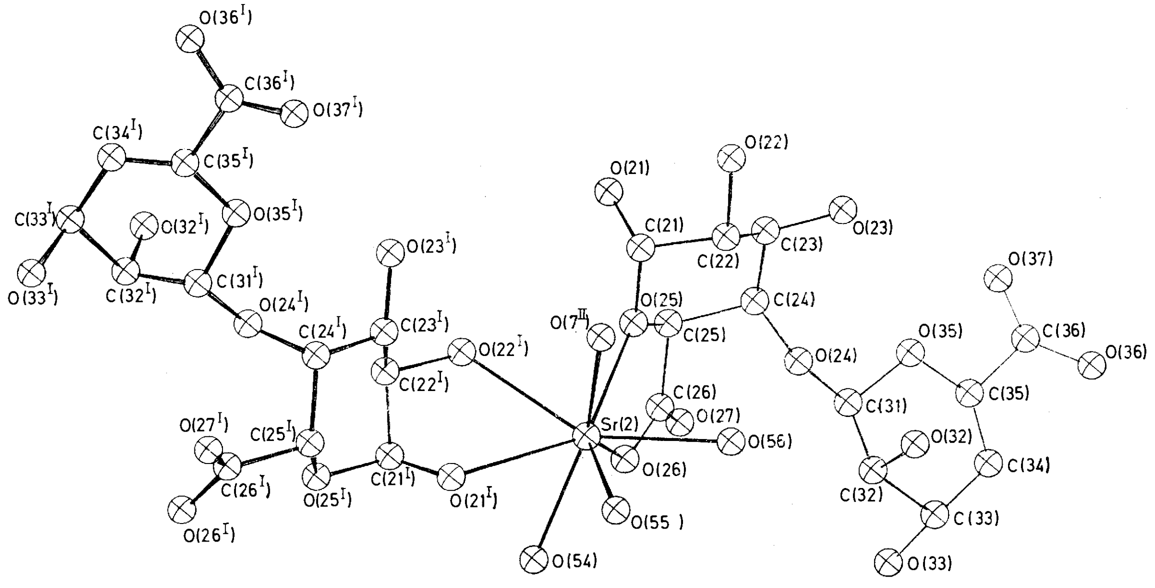

FIGURE 3 Cation co-ordination by the equatorial–axial disaccharide. Symmetry operations are: I, $-1-x, -\frac{1}{2}+y, -z$; II, $-1+x, y, z$

Despite the stereochemical changes which result from the unsaturated sugar ring, the configuration of atoms around the bonds to the glycosidic oxygen in the axial–axial disaccharide appear to be similar to those in the parent polysaccharide. The conformation angles, ϕ and ψ, in this crystal structure might therefore model the

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[14] E. D. T. Atkins, K. D. Parker, E. E. Smolko, and W. Mackie, *Biopolymers*, 1973, **12**, 1879.

stereochemistry of the parent polysaccharide. Using our earlier convention for the definition of the two conformation angles which determine the overall chain-contour,[15] the crystal structure corresponds to ϕ 117°, ψ 158°. This is close to the chain conformation which is stereochemically the most acceptable of the forms which would fit the fibre diffraction data for sodium pectate [15,16] (ϕ 120, ψ 170°; or ϕ 130°, ψ 155°, depending on the assumptions about ring geometry). This is taken as additional confirmation of the (right-handed) chain conformation which we suggested.

Cation Co-ordination.—There are some analogies, but also some differences, between the groups which co-ordinate Sr^{2+} in the present disaccharide structure, and those which co-ordinate cations in the monosaccharide salts examined earlier.[1] These co-ordination geometries are compared in Figures 2—4. In all these situations, O(5) and O(6) of a saturated sugar ring are involved in co-ordination and O(4) is not involved. The involvement of O(5) and O(6) is in line with a general rule which we have already suggested.[1] One axial atom, O(1), participates in co-ordination in the disaccharide salt whereas no axial oxygens are involved in the monosaccharide. The alkaline-earth cations are nine-co-ordinate in the monosaccharide structure, but in the disaccharide structure they are eight-co-ordinate in a distorted square antiprism of a type commonly found in Ca^{2+} salts of hydroxyacids (for a review, see Part I[1]).

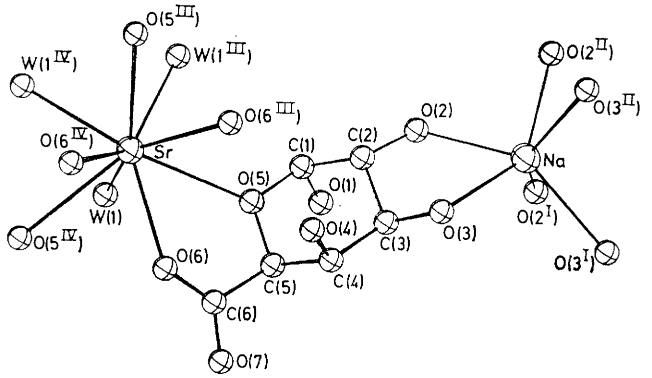
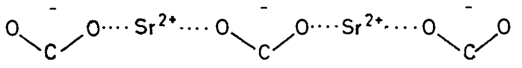


FIGURE 4 Cation co-ordination by sodium strontium galacturonate. Labelling of atoms from ref. 1. Superscripts refer to atoms derived from rotations about the three-fold axis through Na(I and II) or Sr(III and IV)

In the disaccharide structure there are chains which run through the crystal. These involve the carboxylates of saturated residues only. Neither the carboxylate nor any other oxygen function of the unsaturated ring is involved in co-ordination at all This results in an unbalanced charge distribution with an excess of negative charge around the carboxylates of these residues and an excess of positive charge around the strontium ions. This uneven charge distribution and the other unusual features of the structure could perhaps originate from the irregular shape of the digalacturonate ion and consequent difficulty of packing in the crystal. Thus, if the crystal structure is determined by packing of inflexible saturated rings to give maximum co-ordination, the flexible unsaturated rings adapt their conformations and orientations to fill remaining space.



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[5/379 *Received, 24th February,* 1975]

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[15] D. A. Rees and A. W. Wight, *J. Chem. Soc.* (*B*), 1971, 1366.
[16] K. J. Palmer and M. B. Hartog, *J. Amer. Chem. Soc.*, 1945, **67**, 2122.