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Calcium Sodium α-D-Galacturonate Hexahydrate

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Abstract. $CaNa[C_6O_7H_9]_3.6H_2O$, hexagonal, $P6_3$. $a=13{\cdot}498$ (2), $c=9{\cdot}657$ (2) Å, F.W. 750·55, $Z=2$, $V=1523{\cdot}74$ Å^3, $D_x=1{\cdot}636$, $D_m=1{\cdot}665$ g cm^{-3}. The structure was solved by the heavy-atom method, and refined to $R=0{\cdot}040$ for 830 reflexions. The galacturonic acid moiety has the $^4C_1$ chair conformation. The Ca^{2+} ions have nine O atom nearest neighbours in groups of three O(5), O(6) and O(9) atoms at distances of 2·829 (5), 2·397 (6) and 2·423 (7) Å respectively. The Na^+ ions are six-coordinated having two groups of three O atoms each at distances of 2·357 (5) Å for the O(2) and 2·502 (5) Å for the O(3) atoms.

Introduction. The salt was obtained in low yield from an aqueous solution of α-D-galacturonic acid neutralized with $Ca(OH)_2$ to *p*H 6. Samples, recrystallized at 40°C were kindly supplied by Mr B. Larsen of The Institute of Marine Biochemistry of this University. The structure determination, chemical analysis and infrared spectroscopy indicated that the cations were partly Na^+ ions, due to impurities. The rate of crystallization was greatly increased by addition of NaOH besides $Ca(OH)_2$ to the solution. Intensities from a specimen of diameter 0·07 and length 0·48 mm were collected on a Picker FACS-1 four-circle diffractometer with Nb-filtered Mo $K\alpha$ radiation ($\lambda_{\text{Mo }K\alpha}=0{\cdot}71069$ Å). 949 independent reflexions were measured both for hkl and $hk\bar{l}$ by the $\omega/2\theta$ scan technique, with $2\theta_{\text{min}}=3°$ and $2\theta_{\text{max}}=50°$. The scan rate in 2θ was 0·5° min^{-1}. The background was recorded for 40 s on either side of the reflexion. The reflexions 002, 011 and 420 were used as standards, being remeasured at intervals of 30 reflexions. There were no significant changes in the intensities of the standards. The data were corrected for Lorentz, polarization and absorption effects with *TAPSI*1 (Borgen & Mestvedt, 1969). The two sets of $|F_o|$'s were averaged by *FSTAT* (Sivertsen, 1971). 116 observed or unobserved reflexions $[I<2\sigma(I)]$ were rejected; thus 833 reflexions were used for the structure determination. *SCALER* (Hjortås, 1970) was applied for calculating normalized structure factors $E_{\mathbf{h}}$ and their statistical distribution. The values of $|E_{\mathbf{h}}|=0{\cdot}881$ and $|E_{\mathbf{h}}^2-1|=0{\cdot}736$ can be compared with the theoretical values of 0·886 and 0·736 for the non-centrosymmetric case.

Programs from the X-RAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) were used. The Patterson–Harker section indicated Ca(1) on a twofold position $(\frac{2}{3},\frac{1}{3},0)$, and a calculation of F's with these two Ca atoms, with $B=2{\cdot}0$ Å^2, gave $R=0{\cdot}63$ $(R=\sum[||F_o|-K|F_c||]/\sum|F_o|)$. An additional peak at $(0,0,0{\cdot}19)$ appearing in the succeeding E map was taken as Ca(2), leading to $R=0{\cdot}56$. A difference map based on the Ca(1) and Ca(2) positions revealed two peaks corresponding to 4·4 and 5·3 e respectively. These peaks were taken to be O atoms and included. The next map showed peaks of heights 3·6–5·0 e and a six-membered ring structure could be tentatively outlined. All the non-hydrogen atoms could thus successively be included and the refinement with isotropic thermal parameters led to $R=0{\cdot}09$. The thermal parameter of Ca(2) was unusually high, and a refinement of the population factor for this position gave an occupancy of 0·57, corresponding closely to a replacement of Ca by Na. The Ca(2) is also a twofold position, and for Ca^{2+} ions electroneutrality would require that only one half of these positions were occupied. This difficulty is resolved by assuming that Na^+ ions occupy the (2) positions. The least-squares refinement, minimizing the function $\sum w(F_o-KF_c)^2$ with anisotropic thermal parameters for all the heavy atoms gave $R=0{\cdot}05$. A difference map at this stage revealed the positions of the H atoms in peaks corresponding to 0·23–0·45 e. The H atoms bonded to the O(8) water atom could not be located, probably owing to the very high temperature vibrations of O(8). The final refinement cycle with all atoms included gave $R=0{\cdot}040$. The reflexions 100, 110 and 101, which had 2θ's between 3° and 6°, were removed from the data set in the final stage. They had very uneven backgrounds and very large ΔF's. The final results are thus based on 830 observed reflexions.

The atomic coordinates are given in Table 1,† and the thermal parameters in Table 2. Average positional standard deviations are 0·004–0·008 Å for C, O, Na, Ca and 0·06–0·12 Å for H atoms. The scattering factors for all non-hydrogen atoms were those given by Doyle & Turner (1968), and for H by Stewart, Davidson & Simpson (1965).

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† A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31496 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. Some preliminary features of this structure with the nine-coordinated Ca^{2+} ions were reported by Hjortås, Larsen & Thanomkul (1974). A paper on the crystal structures of Ca–Na and Sr–Na galacturonate hexahydrates has recently been published by Gould, Gould, Rees & Scott (1975), who obtained a final R of 12·2% for 837 reflexions for the Ca–Na salt. The agreement between their structure and the present work is fairly good, but some deviations exist; thus C(2)–C(3) and C(5)–C(6) are 1·547 (19) and 1·520 (10) Å in the present work, whereas 1·51 (2) and 1·56 (2) Å respectively were found by Gould *et al.*

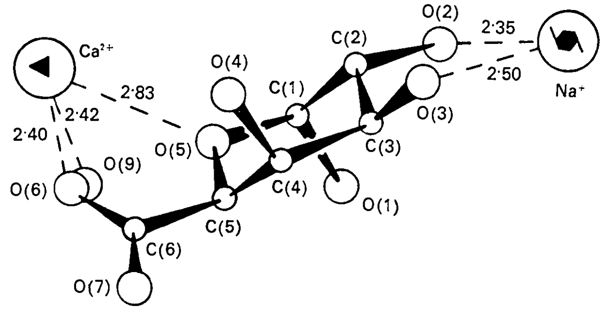

Fig. 1. Projection of Ca–Na α-D-galacturonate along the crystallographic c axis.

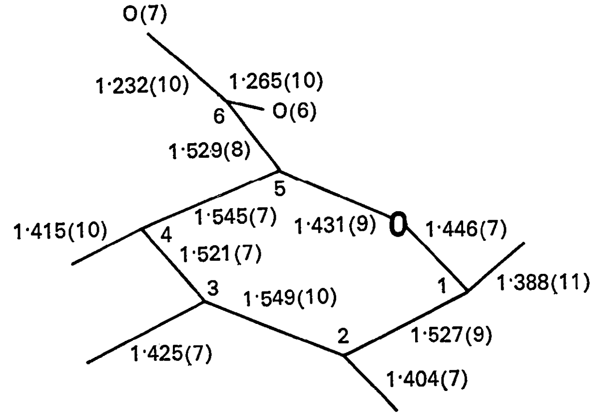

Fig. 2. Bond lengths (Å) between C and O atoms in the α-D-galacturonate moiety.

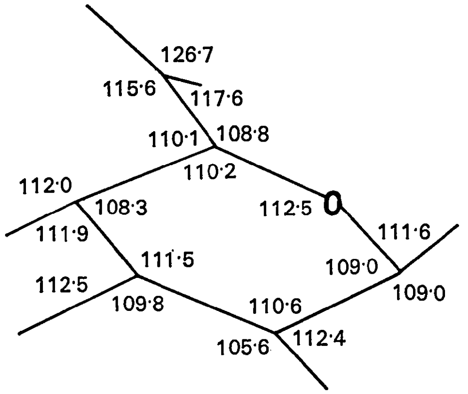

Fig. 3. Bond angles between C–C and C–O bonds in Ca–Na α-D-galacturonate. Average standard deviation is 0·6°.

Table 1. *Fractional coordinates for* Ca–Na *galacturonate hexahydrate with standard deviations in parentheses*

	x	y	z
Ca	0·3333	0·6667	0·9931
Na	1·0000	1·0000	0·8105 (5)
O(1)	0·2868 (4)	0·2839 (4)	1·0804 (6)
O(2)	0·0721 (4)	0·1542 (4)	0·9671 (5)
O(3)	0·1243 (4)	0·1853 (4)	0·6882 (5)
O(4)	0·2505 (4)	0·4281 (4)	0·6709 (5)
O(5)	0·3138 (3)	0·4488 (3)	0·9662 (4)
O(6)	0·4556 (4)	0·6383 (4)	0·8379 (6)
O(7)	0·5477 (4)	0·5581 (4)	0·7389 (6)
O(8)	0·4339 (10)	0·1895 (9)	0·8778 (9)
O(9)	0·3553 (4)	0·8067 (4)	1·1652 (6)
C(1)	0·2329 (5)	0·3407 (5)	1·0287 (7)
C(2)	0·1457 (5)	0·2657 (5)	0·9193 (7)
C(3)	0·2068 (5)	0·2522 (5)	0·7910 (7)
C(4)	0·2984 (5)	0·3676 (5)	0·7361 (7)
C(5)	0·3781 (5)	0·4359 (5)	0·8572 (7)
C(6)	0·4690 (5)	0·5548 (5)	0·8076 (8)
H(C1)	0·192 (5)	0·359 (5)	1·109 (7)
H(C2)	0·099 (4)	0·301 (4)	0·891 (5)
H(C3)	0·243 (6)	0·200 (7)	0·828 (8)
H(C4)	0·349 (5)	0·358 (5)	0·669 (7)
H(C5)	0·411 (4)	0·386 (4)	0·900 (5)
H(O1)	0·333 (6)	0·321 (6)	1·127 (7)
H(O2)	0·023 (7)	0·158 (7)	1·022 (10)
H(O3)	0·097 (7)	0·226 (8)	0·660 (11)
H(O4)	0·223 (11)	0·450 (11)	0·691 (16)
H(O9)*a*	0·332	0·766	1·241
H(O9)*b*	0·412 (7)	0·868 (8)	1·185 (10)

Table 2. *Thermal parameters for* Ca–Na *galacturonate hexahydrate*

U_{ij} ($\times 10^3$) are coefficients in the expression:

$$U=\exp\left[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})\right].$$

E.s.d.'s are given in parentheses for the refined parameters.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca	18 (1)	18 (1)	13 (1)	9 (1)		
Na	23 (1)	23 (1)	27 (2)	12 (1)		
O(1)	27 (3)	20 (2)	32 (3)	4 (2)	−13 (2)	2 (2)
O(2)	25 (2)	18 (2)	26 (3)	1 (2)	12 (2)	1 (2)
O(3)	24 (2)	24 (2)	21 (2)	13 (2)	−5 (2)	−7 (2)
O(4)	34 (3)	23 (2)	21 (2)	16 (2)	−1 (2)	2 (2)
O(5)	19 (2)	14 (2)	16 (2)	6 (2)	4 (2)	0 (2)
O(6)	26 (2)	14 (2)	34 (3)	8 (2)	9 (2)	5 (2)
O(7)	31 (3)	25 (2)	53 (3)	11 (2)	29 (3)	4 (2)
O(8)	216 (11)	125 (8)	66 (6)	123 (8)	49 (6)	39 (5)
O(9)	32 (3)	26 (3)	32 (3)	10 (2)	−4 (2)	−9 (2)
C(1)	25 (3)	16 (3)	22 (3)	10 (2)	3 (2)	−2 (2)
C(2)	17 (3)	21 (3)	22 (3)	10 (3)	5 (3)	−3 (3)
C(3)	16 (3)	14 (3)	18 (3)	4 (2)	−9 (2)	−6 (2)
C(4)	22 (3)	19 (3)	22 (3)	13 (3)	4 (3)	−1 (3)
C(5)	15 (3)	13 (3)	22 (3)	6 (2)	1 (3)	−1 (2)
C(6)	19 (3)	16 (3)	33 (3)	4 (3)	3 (3)	2 (3)

H(C1)	U = 0·022 (17) Å^2	H(O1)	U = 0·025 (23) Å^2
H(C2)	0·001 (12)	H(O2)	0·052 (26)
H(C3)	0·038 (21)	H(O3)	0·067 (31)
H(C4)	0·009 (14)	H(O4)	0·160 (57)
H(C5)	0·000 (12)	H(O9)*a*	0·050
		H(O9)*b*	0·088 (30)

Table 3. *Torsional angles* (°)

Comparison is made with the galactose moiety in α-lactose monohydrate (Fries, Rao & Sundaralingam, 1971) and with average values for 23 pyranose sugars (Arnott & Scott, 1972).

	This structure	Fries *et al.*	Arnott & Scott
O(5)–C(1)–C(2)–C(3)	55·3 (6)	53·7 (3)	56·0 (4·0)
C(1)–C(2)–C(3)–C(4)	−52·8 (6)	−51·4 (3)	−53·2 (3·3)
C(2)–C(3)–C(4)–C(5)	52·4 (6)	54·2 (3)	53·0 (3·3)
C(3)–C(4)–C(5)–C(6)	−58·0 (6)	−59·1 (3)	−55·4 (4·0)
C(4)–C(5)–O(5)–C(1)	64·6 (6)	61·7 (3)	61·1 (3·8)
C(5)–O(5)–C(1)–C(2)	−62·9 (6)	−60·8 (3)	−62·2 (3·3)
O(5)–C(5)–C(6)–O(6)	17·9 (7)	59·4 (3)	

Fig. 1 shows the galacturonate ion viewed along **c**, with the Ca and Na positions indicated. The ion has the $^4C_1$ chair conformation as found in methyl-α-D-galactopyranoside (Gatehouse & Poppleton, 1971) and in methyl-α-D-galacturonic acid methyl ester monohydrate (Hjortås, Larsen, Mo & Thanomkul, 1974). The carboxyl group lies approximately in the O(5)–C(5)–C(6) plane, with O(6) almost *cis* to O(5). The O(5)–C(5)–C(6)–O(6) torsion angle is 17·9°. The bond lengths between heavier atoms are given in Fig. 2; Fig. 3 shows the bond angles. The carboxyl group is in the zwitterion form. C(6)–O(6), 1·263 (10) Å, is only slightly longer than C(6)–C(7), 1·234 (9) Å. The C(1)–O(5) and C(5)–O(5) lengths are 1·448 (6) and 1·430 (8) Å, respectively, thus contrary to the observations in most carbohydrate structures, where C(1)–O(5) is usually shorter than C(5)–O(5) by 0·01–0·02 Å (Jeffrey, Pople & Radom, 1972). The influence of the Ca^{2+} ion, which is coordinated to O(5), might possibly be the reason for this anomaly. It has been observed by Bugg & Cook (1972) that Ca^{2+} ions interacting with carbohydrates can have a marked influence on the bond lengths and angles. The torsion angles of the galactose ring are given in Table 3 and compared with results from other investigations. The largest deviations from previous observations occur for the angles involving O(5). This again supports the assumption that O(5) is influenced by its weak Ca coordination. The coordinations of the Ca^{2+} and Na^+ ions are of special interest. The Ca^{2+} ions are located on a threefold axis and surrounded by three asymmetric units of galacturonate ion and three water molecules. The O coordination of Ca^{2+} consists of three O(6) below, three O(9) above, and three O(5) in approximately the same plane at distances of 2·397 (6), 2·423 (7) and 2·829 (5) Å respectively, forming a tri-capped (or tri-pyramidal) trigonal prism. O(9) belongs to one of the water molecules. The Ca^{2+} ion is outstanding for its variation of O coordination (*Molecular Structures by Diffraction Methods*, 1974). A five-coordinate, distorted trigonal-bipyramidal environment of O atoms for Ca is found in $CaGa_4O_7$, a six-coordinate, octahedral arrangement in γ-$Ca_2Si_2O_4$ and in many oxy- and hydroxy-chlorides, a seven-coordinate, pentagonal-bipyramidal structure in *e.g.* α,α-trehalose $CaBr_2.H_2O$ (Cook & Bugg, 1973*a*), while an eight-coordinate, distorted square antiprism has been most commonly found in complexes of carbohydrates with Ca, *e.g.* in calcium ascorbate dihydrate (Hearn & Bugg, 1974) and in the hydrated calcium bromide salt of lactobionic acid (Cook & Bugg, 1973*b*). A nine-coordinate, trigonal prism environment is found in the hexagonal apatite minerals, in $CaCl_2.6H_2O$ and in aragonite (Dickens & Bowen, 1971). A ten-coordinated Ca position in the structure of β-calcium nitrate dihydrate has been reported by Leclaire (1974). The present structure is, however, the first example of nine-coordination of O around Ca in complexes with carbohydrates. The Ca^{2+} ion is displaced 0·26 Å out of the plane through the three O(5) atoms, this displacement being approximately one half of that found in the apatite structure. The Na^+ ion is surrounded by six hydroxyl O atoms O(2) and O(3) at distances of 2·357 (5) and 2·502 (5) Å respectively. These O atoms form two inverted trigonal pyramids having the Na^+ ion at their apices, with a slight twist around the apex Na^+ ion.

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