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The Crystal Structure of Calcium Ascorbate Dihydrate

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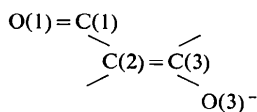
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(Received 21 March 1974; accepted 22 May 1974)

The crystal structure of calcium L-ascorbate dihydrate $\text{Ca}^{2+}(\text{C}_6\text{H}_7\text{O}_6^-)_2 \cdot 2\text{H}_2\text{O}$ has been determined by X-ray diffraction, on an automatic diffractometer with Mo $K\alpha$ radiation. The space group is $P2_1$ with $a=8.335$ (2), $b=15.787$ (3), $c=6.360$ (2) Å and $\beta=107.48$ (1)°. The parameters were refined to $R=0.036$ for 2283 observed reflexions. The average standard deviation in bond lengths is 0.0035 Å for the non-hydrogen atoms. Eight oxygen atoms surround the calcium ion at distances ranging from 2.409 to 2.520 Å, and form a distorted square antiprism. The independent ascorbate anions (*A* and *B*) form stacks which are connected to neighbouring stacks through interactions with calcium ions and water molecules. These anions form tightly bound pairs by short hydrogen bonds between their enediol oxygen atoms, but they are also bonded to each other by normal hydrogen bonds. The geometry of the lactone rings is partly determined by the side chains, which assume different orientations in *A* and *B*. Resonance stabilization of the $\text{O}(1)=\text{C}(1)-\text{C}(2)=\text{C}(3)-\text{O}(3)^-$ group is corroborated.

Introduction

The structural determination of sodium ascorbate (Hvoslef, 1969) revealed significant conformational and bonding changes in comparison with ascorbic acid (Hvoslef, 1968). Studies of infrared and Raman spectra (Hvoslef & Klæboe, 1971) of solids and aqueous solutions as well as circular dichroism measurements (Kresheck, 1968) confirmed these findings. The present study of calcium L-ascorbate dihydrate, $\text{Ca}(\text{C}_6\text{H}_7\text{O}_6)_2 \cdot 2\text{H}_2\text{O}$, was primarily intended to elucidate the conformation of the ascorbate anion under packing conditions different from those in the sodium salt. It was also desirable to verify the bond lengths observed in the conjugated



system of the lactone ring. In this respect the choice of the calcium salt was favourable because it permitted two independent ascorbate anions to be determined simultaneously.

Particular interest is, however, connected with the coordination of calcium ions to sugar molecules, and C. E. Bugg and R. A. Hearn at the University of Alabama have undertaken a simultaneous investigation of this compound in order to obtain additional information of such interactions (see preceding paper).

Experimental

Crystals of calcium L-ascorbate dihydrate $\text{Ca}^{2+}(\text{C}_6\text{H}_7\text{O}_6^-)_2 \cdot 2\text{H}_2\text{O}$ were grown according to the procedure given by Merrill & Ruskin (1947), but satisfactory X-ray data were only obtained from a specimen which had been cut from a large crystal with well developed faces. This fragment was pyramidal with a basal area of 0.034×0.024 cm and a height of 0.020 cm.

The crystal was checked on oscillation and Weissenberg diagrams, and the space group was determined as $P2_1$ from systematic absences ($k=2n+1$ absent in $0k0$) and from the fact that the molecules are optically active. X-ray data were collected on an automatic Picker diffractometer operating in the $\omega-2\theta$ mode. The scan speed was 1°min^{-1} and background counts were 20 s on each side of the Bragg peak. Three reflexions

were used to check the stability of the crystal, but the compound showed no sign of disintegration. With Mo $K\alpha$ radiation ($\lambda=0.7107 \text{ \AA}$) and a limiting 2θ of 60° , a total number of 2297 reflexions were considered. Of these, 2283 were strong enough to be used in the analysis, and were corrected for absorption using a linear absorption coefficient of 4.6 cm^{-1} . Conversion to structure amplitudes and subsequent analyses were made with the programs devised by Dahl, Gram, Groth, Klewe & Rømming (1970) for the CDC 3300 computer.

Unit cell and space group

$a = 8.335 (2) \text{ \AA}$
 $b = 15.787 (3)$
 $c = 6.360 (2)$
 $\beta = 107.48 (1)^\circ$
 Space group $P2_1$
 $Z = 2$

$\text{Ca}(\text{C}_6\text{H}_7\text{O}_6)_2 \cdot 2\text{H}_2\text{O}$
 $M = 426.349$
 $V = 798.2 \text{ \AA}^3$
 $d_{\text{calc}} = 1.778 \text{ g cm}^{-3}$
 $d_{\text{obs}} = 1.75 \text{ g cm}^{-3}$
 $\mu(\text{Mo } K\alpha) = 4.6 \text{ cm}^{-1}$

Structure determination and refinement

The structure was solved by Fourier methods. The calcium position was readily found from Patterson functions (Harker section), and provided an adequate number of phases to localize some of the oxygen atoms which were coordinated to the cation. These atoms were included in a weighted Fourier synthesis which gave information on most of the light atoms. The complication caused by the extra centre of symmetry at the outset was solved by a study of the reasonability of the calcium coordination in conjunction with the R index. As expected, the calcium ion assumes an eight-coordination of oxygen atoms, forming a distorted square antiprism. Least-squares refinement started at $R=0.25$ and improved to $R=0.06$ with isotropic temperature factors only. Inclusion of isotropic hydrogen atoms and anisotropic 'heavy' atoms resulted in a final R value of 0.036 after a few cycles of full-matrix least-squares refinement.

The form factor for Ca^{2+} was from Cromer & Waber (1965), for carbon and oxygen from Hanson, Herman, Lea & Skillman (1964) and for hydrogen from Stewart, Davidson & Simpson (1965). The effects of anomalous scattering for Mo $K\alpha$ radiation for these atoms are small and were neglected in our calculations.

A final difference Fourier map was calculated to detect residual electron density, and six peaks ranging up to a density of 0.5 e \AA^{-3} were observed close to the calcium ion. No other peaks or troughs exceeded 0.2 e \AA^{-3} throughout the unit cell.

A view of the structure is given in Fig. 1. The direction of the c axis is above the plane of the paper, constituting a left-handed crystal system.

The atomic coordinates and their thermal parameters are given in Tables 1 and 2 respectively. Of the two independent anions A and B , the atoms in B are

denoted by asterisks in order to maintain their conventional numbering.†

Discussion

Our analysis will mainly be devoted to the ascorbate moiety; Hearn & Bugg (1974) discuss the calcium-sugar interactions in greater detail.

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30510 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Fractional coordinates for the atoms in calcium ascorbate dihydrate

Standard deviations are in parentheses. The values are multiplied by 10^4 for the heavy atoms and by 10^3 for the hydrogen atoms. Asterisks denote atoms in ascorbate B .

	x^\ddagger	y	z
Ca^{2+}	7869 (1)	0000 (0)	5265 (1)
O(1)	2924 (3)	1066 (2)	214 (4)
O(2)	5899 (3)	1471 (1)	-1091 (4)
O(3)	6117 (3)	3424 (1)	-651 (4)
O(4)	2811 (2)	2445 (1)	970 (4)
O(5)	3343 (3)	3562 (1)	4413 (4)
O(6)	4509 (3)	4951 (2)	3183 (4)
C(1)	3524 (3)	1775 (2)	233 (4)
C(2)	4917 (3)	2052 (2)	-434 (4)
C(3)	5094 (3)	2914 (2)	-180 (4)
C(4)	3810 (3)	3195 (2)	936 (5)
C(5)	4629 (3)	3442 (2)	3361 (5)
C(6)	5635 (4)	4254 (2)	3697 (5)
O(1)*	0819 (3)	3963 (1)	6507 (3)
O(2)*	-961 (3)	3015 (1)	9094 (3)
O(3)*	-2516 (3)	1515 (1)	6050 (4)
O(4)*	58 (3)	2916 (1)	4023 (3)
O(5)*	-1410 (3)	780 (1)	2213 (3)
O(6)*	699 (3)	593 (2)	6164 (3)
C(1)*	64 (3)	3295 (2)	5970 (4)
C(2)*	-875 (3)	2798 (2)	7056 (4)
C(3)*	-1541 (3)	2111 (2)	5778 (4)
C(4)*	-1052 (3)	2188 (2)	3673 (4)
C(5)*	-196 (3)	1446 (2)	2911 (4)
C(6)*	1289 (4)	1069 (2)	4637 (5)
O \mathcal{W} (2)	0570 (3)	4616 (2)	0974 (4)
O \mathcal{W} (1)	5489 (3)	-0092 (2)	1997 (4)
O(2)H	638 (6)	159 (3)	-209 (8)
O(5)H	273 (7)	320 (4)	405 (9)
O(6)H	478 (7)	521 (3)	261 (6)
C(4)H	311 (4)	360 (2)	16 (5)
C(5)H	532 (6)	298 (3)	408 (7)
C(6)H(1)	641 (4)	426 (2)	281 (5)
H(2)	621 (7)	427 (2)	527 (6)
O(2)*H	-176 (7)	319 (4)	918 (9)
O(5)*H	-198 (7)	100 (4)	145 (10)
O(6)*H	79 (7)	77 (4)	714 (9)
C(4)*H	-200 (5)	233 (3)	251 (7)
C(5)*H	019 (4)	162 (2)	173 (5)
C(6)*H(1)	183 (4)	068 (3)	382 (6)
H(2)	204 (5)	152 (3)	541 (6)
O \mathcal{W} (2)H(1)	071 (7)	482 (4)	-016 (11)
H(2)	017 (6)	417 (4)	066 (7)
O \mathcal{W} (1)H(1)	475 (7)	033 (4)	152 (9)
H(2)	515 (7)	-054 (4)	168 (8)

† Hearn & Bugg's parameters (x', y', z') refer to a non-reduced cell. Conversion to our unit cell follows according to: $x = 1 - x'$ (but $-x'$ for ascorbate B); $y = y' - \frac{1}{2}$; $z = \frac{1}{2} - x' + z'$.

Table 2. *Thermal parameters for the atoms in calcium ascorbate dihydrate*

Standard deviations are in parentheses. The values for non-hydrogen atoms are multiplied by 10^5 . Temperature factors are in the form $T = \exp(-B_{11}h^2 - B_{22}k^2 - B_{33}l^2 - B_{12}hk - B_{13}hl - B_{23}kl)$. For the hydrogen atoms the isotropic B values are given.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca	530 (6)	113 (2)	757 (10)	-26 (6)	467 (13)	1 (8)
O(1)	791 (33)	202 (8)	1748 (61)	-247 (26)	535 (72)	-126 (37)
O(2)	1115 (34)	158 (8)	1514 (55)	123 (27)	1540 (73)	-46 (34)
O(3)	779 (29)	173 (8)	1781 (61)	59 (25)	1192 (70)	67 (34)
O(4)	557 (27)	207 (8)	1816 (57)	-54 (24)	856 (65)	-169 (35)
O(5)	829 (30)	181 (7)	1538 (55)	-58 (24)	1239 (67)	-115 (33)
O(6)	1095 (32)	158 (7)	2165 (61)	114 (30)	1699 (74)	259 (41)
C(1)	538 (35)	194 (11)	897 (64)	-21 (32)	99 (75)	-51 (42)
C(2)	670 (37)	150 (9)	908 (62)	54 (31)	449 (77)	-70 (41)
C(3)	497 (34)	163 (10)	871 (61)	102 (30)	400 (74)	15 (40)
C(4)	461 (34)	149 (9)	1254 (67)	109 (30)	477 (80)	-40 (41)
C(5)	552 (34)	157 (9)	1188 (66)	87 (30)	637 (78)	3 (40)
C(6)	663 (38)	201 (11)	1358 (71)	-7 (33)	715 (85)	-164 (45)
O(1)*	882 (31)	173 (7)	1319 (52)	-283 (25)	936 (67)	-175 (33)
O(2)*	683 (29)	260 (5)	932 (46)	-59 (25)	728 (61)	-178 (33)
O(3)*	809 (29)	165 (7)	1499 (52)	-192 (25)	1309 (66)	-144 (32)
O(4)*	886 (30)	161 (7)	986 (48)	-257 (24)	961 (64)	-79 (30)
O(5)*	741 (28)	150 (7)	990 (48)	-77 (24)	298 (59)	-33 (30)
O(6)*	779 (30)	288 (9)	1143 (52)	-203 (28)	184 (63)	285 (36)
C(1)*	504 (35)	162 (10)	833 (62)	34 (31)	348 (77)	45 (40)
C(2)*	494 (34)	159 (9)	801 (59)	-26 (30)	451 (74)	5 (38)
C(3)*	482 (33)	132 (9)	961 (59)	67 (29)	479 (71)	50 (39)
C(4)*	551 (34)	123 (9)	886 (59)	-92 (30)	446 (74)	-21 (37)
C(5)*	610 (36)	155 (9)	874 (61)	-22 (30)	594 (78)	-28 (41)
C(6)*	580 (39)	239 (11)	1400 (74)	30 (34)	557 (87)	254 (48)
OW(2)	1206 (36)	269 (9)	1187 (54)	-133 (32)	629 (73)	-250 (38)
OW(1)	868 (29)	172 (8)	1827 (57)	-89 (27)	-50 (66)	66 (37)

Table 2 (cont.)

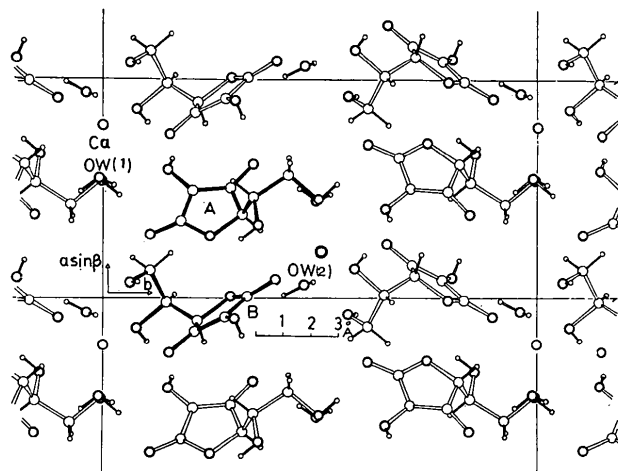


Fig. 1. View of the structure of calcium ascorbate dihydrate along [001]. The reference ions and molecules are indicated by solid lines. The positive direction of c is above the paper.

The calcium coordination

The oxygen atoms surrounding the calcium ion are at distances varying from 2.409 to 2.520 Å, forming a distorted square antiprism. Some distances in this polyhedron are given in Table 3.

Three different ascorbate anions are coordinated to each calcium ion, with three oxygen atoms from ascorbate *B* [O(3)*, O(5)*, O(6)*], two from ascorbate *A* [O(5), O(6)] and one from a symmetry equivalent of

	$B(\text{iso})$
O(2)H	3.8 (1.2)
O(5)H	5.2 (1.6)
O(6)H	6.3 (2.0)
C(4)H	0.5 (1.4)
C(5)H	0.5 (0.8)
C(6)H(1)	0.8 (0.9)
C(6)H(2)	1.5 (1.1)
O(2)*H	5.7 (0.3)
O(5)*H	5.0 (1.6)
O(6)*H	9.9 (2.8)
C(4)*H	2.4 (1.2)
C(5)*H	0.7 (0.9)
C(6)*H(1)	1.6 (1.1)
C(6)*H(2)	1.7 (1.1)
OW(1)H(1)	4.6 (1.9)
OW(1)H(2)	8.5 (2.8)
OW(2)H(1)	5.8 (2.0)
OW(2)H(2)	3.5 (1.7)

B [O(1)*] as may be seen from Fig. 4. The remaining corners of the polyhedron are occupied by the two water molecules. This feature explains the presence of water molecules in the calcium salt. No water is present in the sodium salt.

The ascorbate anions

The interatomic distances and angles in the two independent ascorbate anions are shown in Fig. 2. The average standard deviations are 0.0035 Å and 0.2° respectively. The corrections arising from a rigid-

Table 3. Distances in the polyhedron surrounding the calcium ion

The standard deviation in bond lengths is 0.002 Å for Ca···O and 0.003 Å for O···O.

Bond	Oxygen symmetry code	Distance (Å)
Ca·····O(1)*	1-x, y-½, 1-z	2.427
Ca·····O(3)*	1+x, y, z	2.483
Ca·····O(5)*	1+x, y, z	2.520
Ca·····O(6)*	1+x, y, z	2.441
Ca·····O(5)	1-x, y-½, 1-z	2.518
Ca·····O(6)	1-x, y-½, 1-z	2.466
Ca·····OW(2)	1-x, y-½, 1-z	2.431
Ca·····OW(1)	x, y, z	2.409
O(1)*····O(5)		2.878
O(5)····OW(2)		3.140
OW(2)····O(6)*		2.822
O(6)*····O(1)*		3.134
O(3)*····O(5)*		3.082
O(5)*····OW(1)		2.896
OW(1)····O(6)		3.066
O(6)····O(3)*		3.095

formed, there is a significant deviation from ring planarity, even with respect to the enediol group

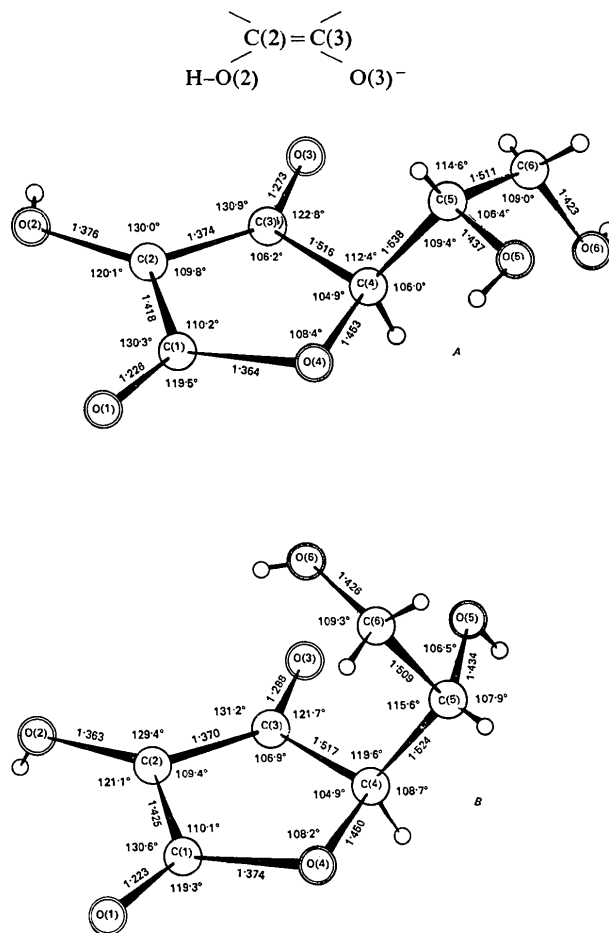


Fig. 2. Perspective drawing of the independent ascorbate anions *A* and *B*. Distances and angles for the non-hydrogen atoms are included in the drawing.

body analysis (Schomaker & Trueblood, 1968) were all within twice these standard deviations, and we consider them to be insignificant.

The present results agree satisfactorily with those found for sodium ascorbate and for the sulphonato-ascorbate anion (McClelland, 1974), except for some instances mentioned below. The assumption of resonance stabilization in the $O(1)=C(1)-C(2)=C(3)-O(3)^-$ system is corroborated, and of course also the function of O(3) in ascorbic acid as the carrier of the protolytic proton. Minor differences in the other hydroxyl groups may be attributed to different environments and the ways in which these groups participate in hydrogen bonding.

The largest difference is in the angular distribution around C(4) which connects the ring and the side chain. This simply reflects the difference in side-chain orientation for the different molecular anions, and it is particularly drastic in calcium ascorbate, as may be seen from Fig. 2. Whereas the geometries of the two side chains are almost identical, the orientation in *B* may be obtained from that in *A* by anti-clockwise rotation around C(5)-C(4) by 117° when the side chain is viewed along C(5)-C(4). The torsional angle O(6)C(6)C(5)O(5) is 47° with O(5) *gauche* to O(6) in either case (Fig. 3), but the particular arrangement in ascorbate *B* allows three of the oxygen atoms [O(3)*, O(5)* and O(6)*] to form a tridentate complex with the calcium ion. The internal repulsions in *B* cause, however, an opening of the C(3)C(4)C(5) and O(4)C(4)C(5) angles to 119.6° and 108.7° compared with 112.4° and 106.0° in ascorbate *A*. The other differences are small and understandable in view of packing conditions and hydrogen bonding.

The difference in the side-chain orientations has some effect on the planarity of the ring systems. In all the determinations of ascorbate anions so far per-

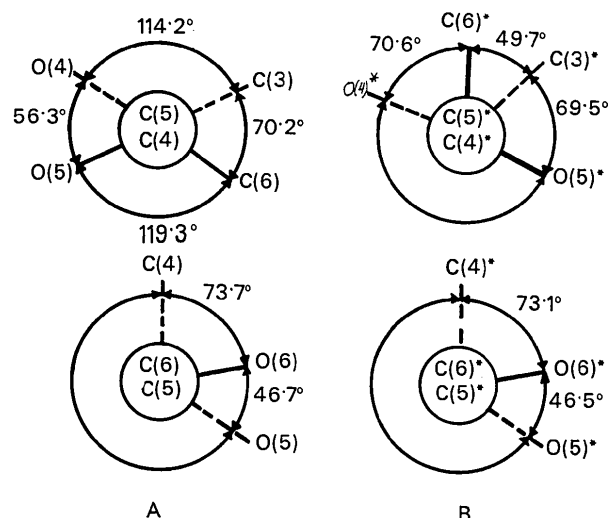


Fig. 3. Torsional angles in the side chains of the ascorbate anions.

indicating a decrease in the sp^2 character of the C(2)–C(3) bond. In the present case, the torsional angles O(3)C(3)C(2)O(2) are 6.8° and 5.4° for *A* and *B* respectively, but the geometry of the rings is different from that in sodium ascorbate. In the latter compound, the entire ring could be described as planar, except for the C(3)–O(3) group. In the calcium salt

C(4) is clearly out of a plane through a slightly corrugated ring system. The deviations of O(4), C(1), C(2) and C(3) from their least-squares plane are negligible, as seen from Table 4. With the exception of C(4), the remaining atoms have very nearly the same relations to the said plane. For C(4), however, the deviation in *A* is opposite to that in *B*, thus reflecting the repulsion mentioned above.

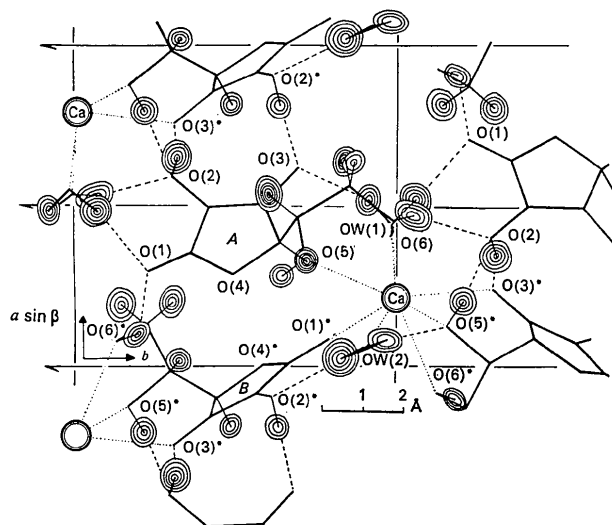


Fig. 4. Composite three-dimensional difference electron density map showing the hydrogen atoms as seen along [001]. Contours start at $0.3 \text{ e } \text{Å}^{-3}$ and are at intervals of $0.05 \text{ e } \text{Å}^{-3}$. Broken lines indicate hydrogen bonds and dotted lines $\text{Ca} \cdots \text{O}$ interactions. Atoms denoted by asterisks belong to ascorbate *B*.

Table 4. Perpendicular distances (Å) from least-squares planes through parts of the ascorbate anions

The atoms marked by † were used to define the planes and were given equal weight in the calculation. C(5) is included in order to clarify the direction of the deviations.

	Ascorbate <i>A</i>	Ascorbate <i>B</i>
O(4)†	0.000	−0.001
C(1)†	0.001	0.003
O(1)†	0.000	−0.001
C(2)†	0.000	−0.001
C(3)	−0.045	−0.039
O(3)	−0.110	−0.109
O(2)	0.088	0.098
C(4)	−0.136	+0.080
C(5)	+0.852	+1.457

Hydrogen bonding

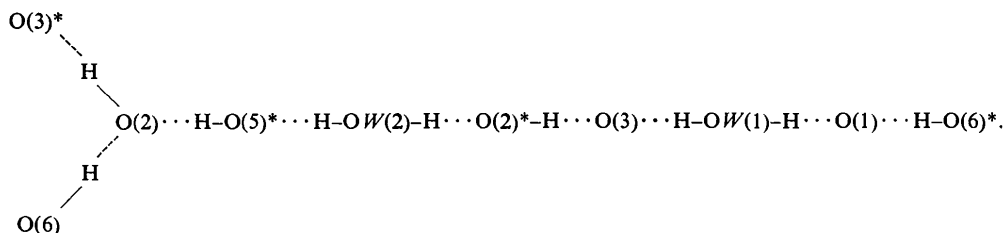
The view in Fig. 1 shows that stacks of ascorbate anions pile up along the $\mathbf{a} + \mathbf{c}$ vector, with their side chains alternately pointing in a direction roughly along or against the direction of the \mathbf{b} axis. These stacks are interconnected by calcium ions and water molecules, and by other hydrogen bonds. The electron density of the hydrogen atoms is shown in Fig. 4, in which can be seen

Table 5. Distances (Å) and angles ($^\circ$) involving hydrogen atoms

Asterisks indicate atoms belonging to ascorbate *B*. Average standard deviations are 0.05 Å and 6° for bonds involving hydrogen atoms and 0.003 Å for the donor–acceptor distances.

	Acceptor symmetry code	O–H	H \cdots O	O \cdots O	O–H \cdots O	C–O–H
O(2)–H \cdots O(3)*	$x+1, y, z-1$	0.87	1.71	2.549	163	122
O(5)–H \cdots O(4)*	x, y, z	} 0.76	2.27	2.862	136	} 107
O(5)–H \cdots O(4)	x, y, z		2.31	2.742	117	
O(6)–H \cdots O(2)	$1-x, y+\frac{1}{2}, -z$	0.63	2.22	2.715	138	107
O(2)*–H \cdots O(3)	$x-1, y, z+1$	0.74	1.84	2.571	171	118
O(5)*–H \cdots O(2)	$x-1, y, z$	0.67	2.14	2.793	169	97
O(6)*–H \cdots O(1)	$x, y, 1+z$	0.66	2.27	2.786	137	117
						H–O–H
OW(2)–H(1) \cdots O(5)*	$-x, y+\frac{1}{2}, -z$	0.83	2.19	2.972	157	} 107
OW(2)–H(2) \cdots O(2)*	$x, y, z-1$	0.78	2.15	2.921	168	
OW(1)–H(2) \cdots O(3)	$1-x, y-\frac{1}{2}, -z$	0.77	1.95	2.707	170	} 104
OW(1)–H(1) \cdots O(1)	x, y, z	0.90	1.89	2.782	170	
	C–H	C(3)–C(4)–H	O(4)–C(4)–H	C(5)–C(4)–H		
C(4)–H	0.91	112	108	113		
C(4)*–H	0.94	109	106	107		
		C(4)–C(5)–H	C(6)–C(5)–H	O(5)–C(5)–H		
C(5)–H	0.96	108	111	108		
C(5)*–H	0.94	110	107	110		
		C(5)–C(6)–H	O(6)–C(6)–H	H(1)–C(6)–H(2)		
C(6)–H(1)	0.97	111	111	} 113		
C(6)–H(2)	0.97	105	107			
C(6)*–H(1)	0.99	105	109			
C(6)*–H(2)	0.97	105	107			

an impressive unbroken chain of $O \cdots O$ interactions involving the following atoms:



The relative strengths of these bonds are indicated by the bond lengths and angles given in Table 5, and the most striking feature is the short hydrogen bonds between the O(2) and O(3) atoms (2.571 and 2.549 Å) which link the independent ascorbates *A* and *B* together in pairs. This observation is in harmony with previous findings in enediols, and may explain the presence of dimers of ascorbates in solution (Forsberg, Johansson, Ulmgren & Wahlberg, 1973). The alcoholic groups form significantly longer hydrogen bonds (2.715–2.862 Å), whereas the water molecules contribute with one set of strong interactions (2.707 and 2.782 Å) and one of weak interactions (2.972 and 2.921 Å).

The hydrogen atom attached to O(5) assumes a quasi-bifurcated position between O(4) and O(4)* at distances of 2.31 and 2.27 Å respectively. The O–H...O angles (137° and 117°) are rather unfavourable for hydrogen bonding, and it is doubtful whether one can consider any of these constellations as hydrogen bonds, especially since oxygen atoms of this type in lactone groups rarely take part in such interactions. We have also noted that the bonds involving O(6)–H are presumably very weak.

The ascorbate anions of each category (*A* and *B*) are tied together by water molecules so that they generate individual helices running in the [010] direction. In addition, the stacks of anions are held together by zigzag chains formed by the O(6)*–H...O(1) and

O(5)*–H...O(2) bonds with a general direction roughly along [001].

We are indebted to B. Holtedahl for the preparation of crystals of calcium ascorbate dihydrate, and to B. Klewe and C. Rømming for technical assistance.

The kind cooperation of Drs Bugg and Hearn is gratefully acknowledged.

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