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Changes in Conformation and Bonding of D-Isoascorbic Acid by Ionization. The Crystal Structure of Sodium D-Isoascorbate Monohydrate

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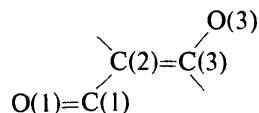
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Sodium D-isoascorbate monohydrate, $C_6H_7O_6Na \cdot H_2O$, is orthorhombic, space group $P2_12_12_1$, with $a = 8.307$ (6), $b = 9.049$ (2), $c = 11.181$ (7) Å, $Z = 4$. The analysis was performed with 703 counter reflexions, the modified tangent formula and two-dimensional cosine invariants. Refinement was by anisotropic full-matrix least squares to a final R of 0.042. There are significant differences between the isoascorbate anion and the free acid. In contrast to the acid, the lactone group of the anion is significantly non-planar. As in isoascorbic acid, the side chain adopts a conformation such that O(6) is at the farthest position from the ring. The OH groups and the water molecule participate in hydrogen bonding. The ring and carbonyl O atoms are not involved in hydrogen bonds and O(3), the protolytic O atom, is an acceptor for four hydrogen bonds. The Na ion is surrounded by six O atoms forming a distorted octahedron with $Na \cdots O$ between 2.296 and 2.386 Å.

Introduction

D-Isoascorbic acid, also known as D-arabinoascorbic acid, is a stereoisomer of L-ascorbic acid with inversion of the OH group at C(5). The structure of D-isoascorbic acid has been determined by Azarnia, Berman & Rosenstein (1971). The analyses of Na L-ascorbate (Hvoslef, 1969) and L-ascorbic acid (Hvoslef, 1968) have revealed significant bonding and conformational changes in the five-membered rings. The enediol group after dissociation of the H atom at O(3) is no longer planar as in the free acid, whereas the lactone group, which is moderately corrugated in the

acid, remains unaffected. It was also shown that the conjugated system of the ring



undergoes significant change on ionization by lengthening of double bonds and shortening of single bonds.

The authors undertook the present analysis to provide data on the molecular shape for comparison with that of D-isoascorbic acid (Azarnia, Berman & Rosen-

Table 1. *Crystal data for sodium D-isoascorbate monohydrate*

Molecular formula	Na ⁺ (C ₆ H ₇ O ₆) ⁻ · H ₂ O	Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Formula weight	216.1	<i>V</i>	840.47 Å ³
Crystal system	Orthorhombic	<i>Z</i>	4
<i>a</i>	8.307 (6) Å	<i>D</i> _m	1.720 g cm ⁻³
<i>b</i>	9.049 (2)	<i>D</i> _x	1.723
<i>c</i>	11.181 (7)	μ(Mo <i>K</i> α)	2.13 cm ⁻¹
Systematic absences	<i>h</i> 00, <i>h</i> = 2 <i>n</i> + 1 0 <i>k</i> 0, <i>k</i> = 2 <i>n</i> + 1 00 <i>l</i> , <i>l</i> = 2 <i>n</i> + 1	Crystal dimensions	0.5 × 0.3 × 0.3 mm
		λ(Mo <i>K</i> α)	0.71069 Å

stein, 1971), to see whether ionization of the latter is accompanied by changes of the molecular shape similar to those of L-ascorbic acid (Hvoslef, 1968).

Experimental

Crystals were grown from an aqueous solution by slow evaporation at room temperature. Intensities were collected on a Nonius CAD-3 diffractometer with Zr-filtered Mo *K*α radiation (λ = 0.71069 Å) and the ω-scan technique. The crystallographic data are summarized in Table 1.

923 reflexions were measured over one octant of the sphere of reflexion. The upper limit for sin θ/λ was 0.64 Å⁻¹. Equivalent reflexions were averaged to give 809 independent reflexions. Of these, 703 were above the 2.5σ(*I*) level. Lorentz and polarization corrections were applied. No corrections were made for absorption or extinction.

Structure determination and refinement

The structure was solved by direct methods. The observed structure factors were scaled by means of a Wilson (1942) plot. The scattering factors used for C, O and Na were those of Cromer & Mann (1968) and for H those of Stewart, Davidson & Simpson (1965). O(3) was assumed to be the carrier of the negative charge of the anion.

Initially attempts were made to solve the structure with the *MULTAN* program of the X-RAY system (1972), and 188 normalized structure factors having |*E*| > 1.2. However, it was not possible to recognize even a partial structure from *E* maps computed with any of the sets generated by the tangent refinement; values for the absolute figures of merit ranged from 0.83 to 1.32 and for *R*_{Karle} from 0.31 to 0.40. The structure was eventually solved with a set of programs of Weeks, Pokrywiecki & Edmonds (1973). These programs differ from direct-method programs available in the X-RAY system (1972) in that emphasis is placed on the central role played by the universal cosine structure invariants, cos(φ_{h₁} + φ_{h₂} + φ_{h₃}), in phase determination. To find a basic set of phases we started with 74 projec-

tion reflexions with |*E*| > 1.0. These reflexions have restricted phases in *P*2₁2₁2₁. Together they yielded 160 triple products having *A* > 0.5, where *A* = 2*N*^{-1/2}|*E*_{*H*}*E*_{*K*}*E*_{*H*+*K*}|. Four reflexions were selected for defining the origin and fixing the enantiomorph (Table 2).

The phases of 39 reflexions could be determined to form the basic set and with the aid of the modified tangent formula (Hauptman & Weeks, 1972) 157 phases of general reflexions could now be determined. The phases of three reflexions of the starting set changed 180°. In the *E* map calculated with these 157 reflexions, the 20 highest peaks matched the Na, six C and seven O atoms.

Anisotropic block-diagonal least-squares refinement of the Na, C and O positional parameters gave *R* =

Table 2. *Origin and enantiomorph-defining phases*

Reflexion	<i>E</i>	Phase	Type
0 4 3	2.12	0	Origin
3 0 3	1.92	π/2	Origin
10 3 0	1.64	0	Origin
1 0 6	1.60	0	Enantiomorph

Table 3. *Fractional coordinates (×10⁴) of the non-hydrogen atoms*

The estimated deviations are in parentheses and refer to the last decimal position.

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	476 (6)	4171 (6)	6949 (4)
C(2)	-1116 (6)	3791 (6)	6612 (4)
C(3)	-2167 (5)	4230 (5)	7477 (4)
C(4)	-1191 (6)	4907 (6)	8482 (4)
C(5)	-1250 (6)	4078 (6)	9665 (4)
C(6)	-936 (7)	2447 (6)	9480 (5)
O(1)	1760 (4)	3946 (4)	6446 (3)
O(2)	-1507 (4)	3049 (4)	5591 (3)
O(3)	-3727 (4)	4122 (4)	7535 (3)
O(4)	468 (4)	4888 (4)	8039 (3)
O(5)	-35 (4)	4656 (4)	10426 (3)
O(6)	-1149 (6)	1648 (5)	10584 (4)
O(<i>W</i>)	296 (4)	3510 (4)	3619 (3)
Na	2620 (2)	4440 (2)	4536 (2)

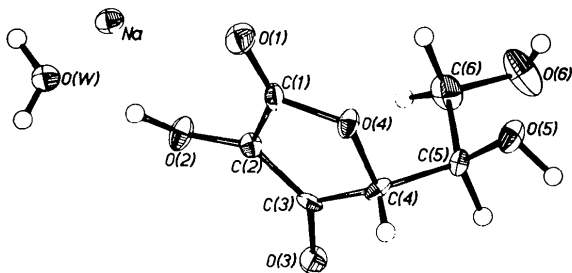


Fig. 1. Molecular conformation and atomic numbering of sodium D-isoascorbate monohydrate. C, O and Na are represented by thermal ellipsoids at the 50% level of probability.

Table 4. Fractional coordinates ($\times 10^3$) and isotropic thermal parameters of the hydrogen atoms

	x	y	z	B (\AA^2)
H(C4)	-140 (6)	588 (5)	859 (4)	1.0
H(C5)	-244 (6)	429 (5)	1001 (4)	1.0
H(C6)	-160 (6)	190 (6)	886 (5)	2.2
H'(C6)	37 (7)	233 (6)	914 (5)	2.2
H(O2)	-81 (6)	326 (6)	492 (4)	1.6
H(O5)	-68 (6)	506 (6)	1103 (4)	1.4
H(O6)	-41 (7)	164 (6)	1084 (5)	2.7
H(O W)	61 (6)	276 (6)	319 (4)	1.5
H'(O W)	-19 (6)	415 (6)	329 (4)	1.5

0.072 for 703 reflexions. At this stage the eight strongest low-order reflexions, which apparently suffered from extinction, were excluded from the calculations. A difference synthesis yielded the positions of the nine H atoms (electron density range 0.25–0.52 $e \text{\AA}^{-3}$) which were included in the refinement with constant thermal parameters equal to those of the carrier atoms. Full-matrix refinement resulted in a final R of 0.042 ($R = \Sigma |F_o| - |F_c| / \Sigma |F_o|$) and $R_w = 0.049$ ($R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w^2]^{1/2}$; $w = \sigma^{-2}(F_o)$). The 'goodness-of-fit' is 3.85; the maximal shift/error ratio is 0.38 for the non-hydrogen and 0.71 for the H atom parameters. In a final difference synthesis the highest electron density was 0.22 $e \text{\AA}^{-3}$. The positional parameters of the non-hydrogen atoms are given in Table 3, those of the H atoms in Table 4.* The atomic numbering is shown in Fig. 1, plotted with ORTEP (Johnson, 1965).

Discussion of the structure

The isoascorbate anion

In Table 5 the bond distances and angles of the isoascorbate anion are compared with the values reported

for isoascorbic acid (Azarnia, Berman & Rosenstein, 1971). The differences in corresponding distances and angles in L-ascorbic acid (Hvoslef, 1968) and sodium L-ascorbate (Hvoslef, 1969) are also tabulated. It is seen that nearly the same bonding and angular changes occur on ionization of D-isoascorbic acid and L-ascorbic acid.

The conjugated system O(1)=C(1)–C(2)=C(3)–O(3) has undergone a considerable change, by a shortening of the single and a lengthening of the double bonds. C(2)–O(2) and C(3)–C(4) have also been lengthened and this is probably caused by a change of hybridization at C(2) and C(3), as has been suggested by Hvoslef (1969) for Na L-ascorbate. The significant changes in the angular arrangement about some of the ring C atoms possibly relate to this change in hybridization. The most striking difference is found in the

Table 5. Comparison of bond distances (\AA) and angles ($^\circ$), in sodium isoascorbate monohydrate and isoascorbic acid

The estimated standard deviations are in parentheses.

	Sodium iso- ascor- bate . H ₂ O	Isoascorbic acid*	Difference	
C(1)–O(1)	1.222 (6)	1.200 (5)	+0.022	+0.017†
C(2)–O(2)	1.364 (6)	1.340 (6)	+0.024	+0.023
C(3)–O(3)	1.301 (6)	1.329 (4)	–0.028	–0.039
C(1)–O(4)	1.381 (6)	1.365 (6)	+0.016	+0.003
C(4)–O(4)	1.465 (6)	1.437 (4)	+0.028	+0.004
C(5)–O(5)	1.420 (6)	1.416 (6)	+0.004	–0.017
C(6)–O(6)	1.441 (7)	1.428 (7)	+0.013	–0.008
C(1)–C(2)	1.418 (7)	1.446 (5)	–0.028	–0.036
C(2)–C(3)	1.362 (7)	1.331 (6)	+0.031	+0.035
C(3)–C(4)	1.516 (7)	1.493 (4)	+0.023	+0.023
C(4)–C(5)	1.521 (7)	1.531 (5)	–0.010	+0.015
C(5)–C(6)	1.513 (8)	1.520 (6)	–0.007	–0.018
C(4)–O(4)–C(1)	108.0 (4)	109.6 (2)	–1.6	–1.1
O(4)–C(1)–C(2)	110.1 (4)	109.4 (3)	+0.7	+1.1
C(1)–C(2)–C(3)	109.8 (4)	107.1 (4)	+2.7	+1.7
C(2)–C(3)–C(4)	107.5 (4)	110.9 (3)	–3.4	–3.7
C(3)–C(4)–O(4)	104.4 (3)	102.9 (2)	+1.5	+1.2
O(4)–C(1)–O(1)	119.2 (4)	121.7 (3)	–2.5	–1.0
O(1)–C(1)–C(2)	130.6 (4)	128.8 (4)	+1.8	–0.1
C(1)–C(2)–O(2)	124.4 (4)	124.5 (3)	–0.1	–3.0
O(2)–C(2)–C(3)	125.8 (4)	128.4 (3)	–2.6	+1.2
C(2)–C(3)–O(3)	130.7 (4)	132.8 (4)	–2.1	–2.2
O(3)–C(3)–C(4)	121.7 (4)	116.3 (4)	+5.4	+5.8
C(3)–C(4)–C(5)	115.3 (4)	114.0 (3)	+1.3	+1.3
O(4)–C(4)–C(5)	108.6 (4)	111.7 (3)	–3.1	–0.1
C(4)–C(5)–O(5)	108.4 (4)	108.2 (3)	+0.2	+1.7
C(4)–C(5)–C(6)	110.9 (4)	112.5 (4)	–1.6	–2.6
O(5)–C(5)–C(6)	108.6 (4)	111.6 (3)	–3.0	+1.4
C(5)–C(6)–O(6)	110.6 (4)	110.9 (3)	–0.3	+0.5

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32368 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* Azarnia, Berman & Rosenstein (1971).

† This column gives the differences between the corresponding bond distances (\AA) and angles ($^\circ$) in sodium ascorbate (Hvoslef, 1969) and ascorbic acid (Hvoslef, 1968).

angle O(3)—C(3)—C(4) which is opened by 5.4° , in good agreement with the opening of 5.8° in Na L-ascorbate (Hvoslef, 1969).

The C—C distances agree with the accepted values for different hybridizations (Stoicheff, 1962). The large difference (0.084 \AA) in the C—O lengths involving the O atom of the ring has also been observed in other ascorbates and isoascorbates (Table 6) and may be because of a valence resonance form of the lactone group (MacDonald & Alleyne, 1963; Hvoslef, 1968).

The ring angles at the C atoms range from 104.4 to 110.1° ; the range in isoascorbic acid is 102.9 – 110.9° . The C—H distances range from 0.91 to 1.16 \AA , mean $1.04 (5) \text{ \AA}$; for the O—H distances the range is 0.68 – 0.97 \AA , mean $0.85 (5) \text{ \AA}$. The bond angles involving H atoms range from 100 to 118° , mean $109 (3)^\circ$.

The ring system of the isoascorbate anion comprises the lactone group and the enediol group. In contrast to isoascorbic acid, where the lactone group is exactly planar and the enediol group less so, both groups in the isoascorbate anion strongly deviate from planarity (Table 7). The best planes through the lactone group and the enediol group are at only 1.4° to each other. The ring system consisting of the eight atoms of the lactone and enediol groups is non-planar: the r.m.s. deviation from the best plane is 0.026 \AA ; for isoascorbic acid the r.m.s. deviation is 0.016 \AA (Azarnia, Berman & Rosenstein, 1971).

Comparison of the planarity of the lactone and enediol groups of the pair ascorbic acid, Na ascorbate (Table 7) reveals that in ascorbic acid the enediol group of the two independent molecules is planar and sig-

Table 6. *Endocyclic C—O bond distances (Å) and the valence-ring O angle (°) in sodium isoascorbate monohydrate and related compounds*

Compound	C(1)—O(4)	O(4)—C(4)	Difference	C(1)—O(4)—C(4)	
Na D-isoascorbate · H ₂ O	1.381	1.465	0.084	108.0	This paper
D-Isoascorbic acid	1.365	1.437	0.072	109.6	Azarnia, Berman & Rosenstein (1971)
Na L-ascorbate	1.358	1.448	0.090	108.0	Hvoslef (1969)
L-Ascorbic acid*	1.355	1.444	0.089	109.1	Hvoslef (1968)
Ca L-ascorbate · 2H ₂ O*	1.371	1.455	0.084	107.6	Hearn & Bugg (1974)
Ca L-ascorbate · 2H ₂ O*	1.369	1.452	0.083	108.3	Hvoslef & Kjellevoid (1974)
Tl ^I L-ascorbate*	1.38	1.48	0.10	105	Hughes (1973)
Ba 2-O-sulfonato-L-ascorbate · 2H ₂ O	1.376	1.455	0.079	108.4	McClelland (1974)

* The values given are averages for the two independent molecules.

Table 7. *Distances (Å) from the best planes through parts of the ring system in sodium isoascorbate monohydrate and some related compounds*

Lactone group	Sodium iso-	Isoascorbic	Sodium	Ascorbic acid ^(d)	
	ascorbate · H ₂ O ^(a)	acid ^(b)	ascorbate ^(c)	Molecule A	Molecule B
C(1)	0.0105	0.0005	0.0145	0.0110	0.0008
C(2)	0.0122	0.0000	−0.0116	0.0025	−0.0139
O(1)	−0.0261	−0.0004	0.0034	−0.0127	0.0192
O(4)	0.0351	0.0002	−0.0202	0.0113	−0.0346
C(4)	−0.0317	−0.0003	0.0140	−0.0122	0.0285
Enediol group					
O(2)	−0.0228	−0.0136	−0.0131	−0.0008	−0.0034
C(2)	0.0296	0.0154	0.0193	0.0014	0.0047
C(3)	0.0120	0.0132	0.0217	−0.0004	−0.0008
C(4)	−0.0179	−0.0122	−0.0172	−0.0004	−0.0024
O(3)	−0.0008	−0.0028	−0.0048	0.0002	0.0002
Ring atoms					
C(1)	−0.0135	0.0032	−0.0004	−0.0064	0.0164
C(2)	−0.0042	−0.0094	0.0406	0.0077	0.0047
C(3)	0.0184	0.0114	−0.0618	−0.0060	−0.0215
C(4)	−0.0251	−0.0087	0.0608	0.0019	0.0297
O(4)	0.0244	0.0035	−0.0391	0.0028	−0.0292

^(a) This paper. ^(b) Azarnia, Berman & Rosenstein (1971). ^(c) Hvoslef (1969). ^(d) Hvoslef (1968).

Table 8. *Endocyclic torsion angles (°) of sodium isoascorbate monohydrate and some related compounds*The torsion angle $A(1)-A(2)-A(3)-A(4)$ is viewed along $A(2)-A(3)$ with a clockwise rotation of $A(1)$ to $A(4)$ taken to be positive.

	Sodium	Isoascorbic	Sodium	Ascorbic acid ^(d)	
	isoascorbate · H ₂ O ^(a)	acid ^(b)	ascorbate ^(c)	Molecule A	Molecule B
C(1)–C(2)–C(3)–C(4)	–2.0	–2.0	–9.3	–1.3	–2.4
C(2)–C(3)–C(4)–O(4)	+3.9	+1.9	+11.5	+0.8	+4.8
C(3)–C(4)–O(4)–C(1)	–4.5	–1.1	–9.0	+0.1	–5.4
C(4)–O(4)–C(1)–C(2)	+3.5	+0.0	+3.5	–0.9	+4.3
O(4)–C(1)–C(2)–C(3)	–0.9	+1.3	+4.1	+1.4	–1.2

^(a) This paper. ^(b) Azarnia, Berman & Rosenstein (1971). ^(c) Hvoslef (1969). ^(d) Hvoslef (1968).

nificantly non-planar in the ascorbate anion, whereas the planarity of the lactone group of the ascorbate anion is intermediate between that of the lactone groups of the two independent molecules of the acid. This is contrary to the results reported for Na ascorbate (Hvoslef, 1969, Table 6), which state that the lactone group of the anion is planar within 3σ . The corrected values given in Table 7 are based on recalculations of the best plane of the lactone group of the ascorbate anion.

The effect of ionization on the conformation of the ring of isoascorbic and ascorbic acids is best demonstrated by the change of the planarity of the ring atoms and of the endocyclic torsion angles. As Tables 7 and 8 show, the ionization of ascorbic acid is accompanied by a pronounced distortion of the ring, whereas the distortion of isoascorbic acid is only moderate.

The conformation of the side chain

C(4), C(5), C(6) and O(6) of the side chain form an extended, roughly planar zigzag chain in which each atom is within 0.03 \AA of the plane. The angle between this plane and that of the ring is 86.9° .

The conformation about C(4)–C(5) (Fig. 2) is such that the unfavourable 1,3-vicinal (*peri*) interaction (Jeffrey & Kim, 1970) between O(5) or C(6) and O(3) is avoided, requiring H(C5) to be antiparallel to O(4). The only exception to this arrangement [which is also found in ascorbic acid and its Na salt (Hvoslef, 1969), isoascorbic acid (Azarnia, Berman & Rosenstein, 1971) and in the two independent molecules in the structure of Tl ascorbate (Hughes, 1973)] is found in Ca ascorbate (Hearn & Bugg, 1974; Hvoslef & Kjellefold, 1974). In this structure, O(5) and O(3) of one of the two independent molecules are antiparallel, thus constituting the rare, unfavourable 1,3-vicinal interaction.

Relative to isoascorbic acid, the conformation about C(4)–C(5) of the anion has become more staggered by a rotation of 31° . A similar change applies to the conformation about C(5)–C(6) (Fig. 2), in which O(6) by a rotation of 8° has become nearly *gauche* relative to O(5), the deviation from the ideal staggered conformation being 5.5° . Though the positions of O(6) in

ascorbic and isoascorbic acids are necessarily different, O(6) is in the staggered conformation that takes it farthest from the ring in both these acids and their Na salts.

Coordination of the sodium ion

Each Na ion is coordinated to six O atoms (Fig. 3) belonging to four different isoascorbate anions and the water molecule. O(3) does not participate in the Na coordination. This is not surprising in view of the four-fold participation of this atom in hydrogen bonding (see below). The polyhedron of the six O atoms is a distorted octahedron (Table 9). However, the distortion is much less than that in Na ascorbate (Hvoslef, 1969), as follows from both the narrow range of $\text{Na} \cdots \text{O}$ distances, $2.296\text{--}2.386 \text{ \AA}$ for Na isoascorbate compared to $2.416\text{--}2.725 \text{ \AA}$ for Na ascorbate, and the mean deviations of the polyhedron angles that amounts to 9°

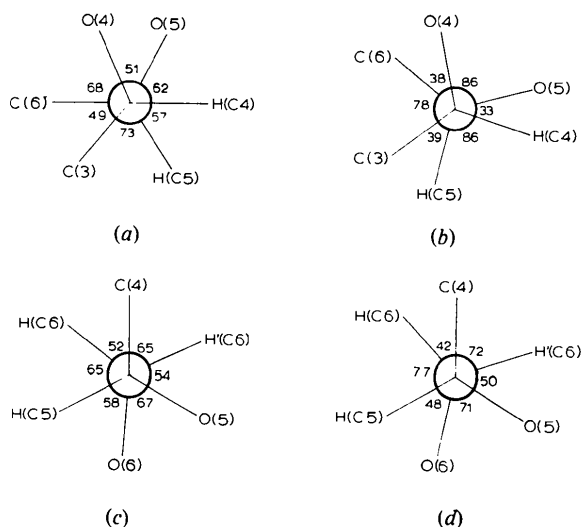


Fig. 2. Torsion angles ($^\circ$) of the side chains of sodium D-isoascorbate monohydrate and D-isoascorbic acid. Newman projections show the dihedral angles about C(4)–C(5) in (a) sodium D-isoascorbate monohydrate and (b) D-isoascorbic acid, and about C(5)–C(6) for the same compounds in (c) and (d) respectively.

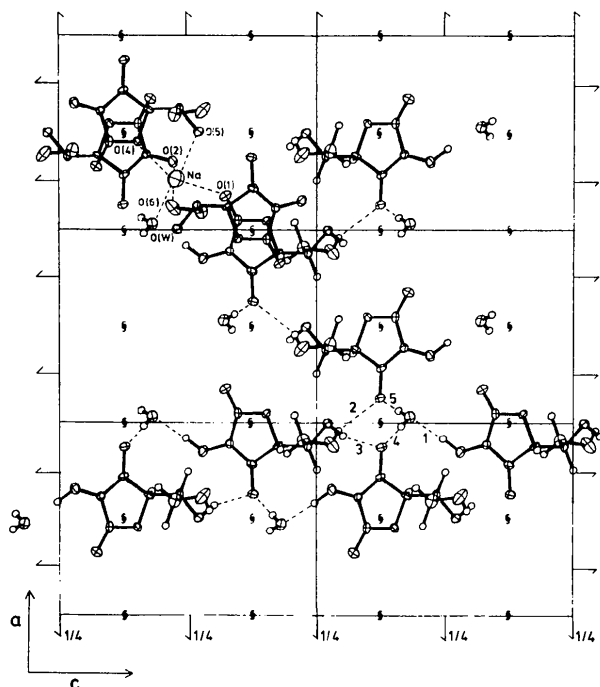


Fig. 3. A composite view of the structure of sodium D-isoascorbate monohydrate down the *b* axis. Hydrogen bonds, numbered according to Table 10, are indicated by dashed lines as well as the sodium coordination. For several molecules the H atoms are omitted.

in Na isoascorbate and 19° in Na ascorbate. Na, O(2'), O(5''), O(6''') and O(W) form an equatorial plane (r.m.s. deviation 0.013 \AA) with O(1) and O(4'') at the remaining corners of the octahedron.

Hydrogen bonding

The hydrogen bonds are shown in Fig. 3, and their geometry is given in Table 10. The three OH groups of the isoascorbate anion and both OH groups of the water molecule are engaged in a hydrogen-bond pattern that involves all the O atoms with the exception of carbonyl O(1) and ring O(4). The water molecule accepts one hydrogen bond and the only other acceptor is O(3), which accepts four. The isoascorbate anions and water molecules are connected by hydrogen bonds along *a* and *c*. The water molecule is bonded to three symmetry-related isoascorbate anions and two donating hydrogen bonds of O(5) and O(6) complete the scheme.

The unique property of O(3), in accepting no less than four hydrogen bonds, is certainly correlated with the fact that it carries the negative charge of the anion. In this respect it is interesting to examine its hydrogen-bond accepting capacity in other (iso)ascorbate anions. In three anions, *viz* Na ascorbate (Hvoslef, 1969), Ca ascorbate (Hvoslef & Kjellefold, 1974) and Tl ascor-

Table 9. Bond distances (\AA) and angles ($^\circ$) in the distorted octahedron surrounding sodium

Primes represent different equivalents of the reference atoms. Estimated standard deviations are given in parentheses.

Na—O(1)	2.296 (4)	Na—O(4'')	2.386 (4)	Na—O(6''')	2.347 (5)
Na—O(2')	2.370 (4)	Na—O(5'')	2.383 (4)	Na—O(W)	2.342 (4)
O(1)—Na—O(2')	88.1 (1)	O(2'')—Na—O(4'')	89.8 (1)	O(4'')—Na—O(6''')	95.1 (2)
O(1)—Na—O(4'')	155.4 (1)	O(2'')—Na—O(5'')	95.4 (1)	O(4'')—Na—O(W)	109.5 (1)
O(1)—Na—O(5'')	86.6 (1)	O(2'')—Na—O(6''')	164.8 (2)	O(5'')—Na—O(6''')	99.8 (2)
O(1)—Na—O(6''')	93.2 (2)	O(2'')—Na—O(W)	83.4 (1)	O(5'')—Na—O(W)	178.2 (2)
O(1)—Na—O(W)	94.6 (1)	O(4'')—Na—O(5'')	69.2 (1)	O(6''')—Na—O(W)	81.5 (2)

Table 10. Distances (\AA) and angles ($^\circ$) involving hydrogen bonds in sodium isoascorbate monohydrate

No.	Hydrogen bond	O—H	H...O	O...O	O—H...O	Symmetry operation*
1	O(2)—H(O2)...O(W')	0.97 (5)	1.74 (5)	2.699 (5)	169 (5)	555.1
2	O(5)—H(O5)...O(3')	0.94	1.90	2.801	160	465.2
3	O(6)—H(O6)...O(3')	0.68	2.39	2.993	149	557.3
4	O(W)—H(OW)...O(3')	0.87	1.97	2.828	169	556.3
5	O(W)—H'(OW)...O(3')	0.79	2.00	2.785	174	464.2

* The symmetry operation is performed on atom O'. The first set of numbers specifies the lattice translations, *e.g.* 465.2 is $-a + b$ from 555.2. The last digit indicates one of the following symmetry operations: (1) x, y, z ; (2) $\frac{1}{2} - x, -y, \frac{1}{2} + z$; (3) $\frac{1}{2} + x, \frac{1}{2} - y, -z$; (4) $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

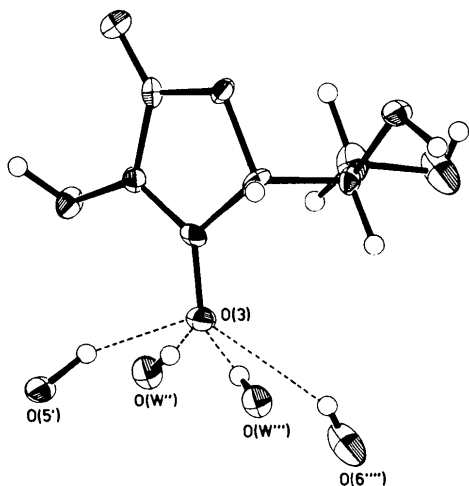


Fig. 4. The hydrogen-bond configuration around O(3). The symmetry code is: (') $-x - \frac{1}{2}, -y + 1, z - \frac{1}{2}$; (") $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (""') $-x - \frac{1}{2}, -y + 1, z + \frac{1}{2}$; (""") $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 2$.

bate (Hughes, 1973), O(3) accepts only one hydrogen bond, but these bonds have in common that the donor-acceptor distances are very short: in Na ascorbate 2.546 Å, in Ca ascorbate (two independent molecules) 2.549 and 2.571 Å, and in Tl ascorbate (two independent molecules) 2.61 and 2.63 Å. The short O...O contacts imply that O(3) has a very large hydrogen-bond accepting capacity in these structures. It seems justified to conclude that in Na isoascorbate this capacity, instead of being used to form a short hydrogen bond, is employed in accepting an unusually large number of hydrogen bonds. It is not surprising that on the average the O...O distances fall somewhat outside the range that is considered normal for a hydrogen bond. The arrangement of O(3) is shown in Fig. 4. Two water molecules each donate a hydrogen

bond, and together with O(6)-H and O(5)-H of the side chain a distorted pyramidal coordination of O(3) is achieved. The four donating O atoms form a rather corrugated equatorial plane with a r.m.s. deviation of 0.27 Å, the distance of O(3) to this plane is 1.28 Å.

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