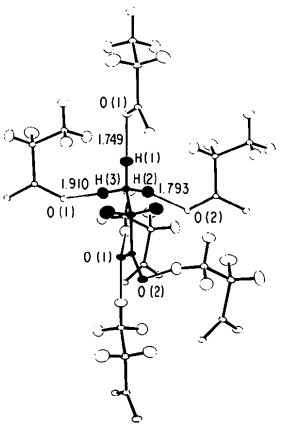

Fig. 4. An illustration of the six hydrogen bonds around one molecule.

83 K] is found between the N atom and the O(1) atom $(-y, x-y, \frac{2}{3}+z)$. This contact is not classified as a hydrogen bond since the three O···H distances [O(1)···H(1) 2·827 (2), O(1)···H(2) 2·532 (2), O(1)···H(3) 2·771 (2) Å] all are well within the range of normal van der Waals contacts. Another electrostatic interaction is found between the N atom and the O(2) atom at $(-y, x-y-1{\cdot}0, \frac{2}{3}+z)$ with a separation of 3·017 (2) Å [O(2)···H(1) = 2·847 (2), O(2)···H(3) = 2·659 (2) Å].

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X-ray Studies on Crystalline Complexes Involving Amino Acids. IV. The Structure of L-Arginine L-Ascorbate*

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Abstract

L-Arginine ascorbate, $C_6H_{15}N_4O_2^+.C_6H_7O_6^-$, a 1:1 crystalline complex between the amino acid arginine and the vitamin ascorbic acid, crystallizes in the monoclinic space group $P2_1$ with two formula units in a cell of dimensions $a = 5{\cdot}060\ (8)$, $b = 9{\cdot}977\ (9)$, $c = 15{\cdot}330\ (13)$ Å, $\beta = 97{\cdot}5\ (2)°$. The structure was solved by the symbolic addition procedure and refined to an R of 0·067 for 1501 photographically observed reflec-

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tions. The conformation of the arginine molecule in the structure is different from any observed so far. The present structure provides the first description of the ascorbate anion unaffected by the geometrical constraints and disturbances imposed by the requirements of metal coordination. The lactone group and the deprotonated enediol group in the anion are planar and the side chain assumes a conformation which appears to be sterically the most favourable. In the crystals, the arginine molecules and the ascorbate anions aggregate separately into alternating layers. The molecules in the arginine layer are held together by interactions involving α-amino and α-carboxylate groups, a situation analogous to that found in proteins. The two layers of unlike molecules are interconnected primarily through the interactions of the side-chain guanidyl group of arginine with the ascorbate ion. These involve a specific ion-pair interaction accompanied by two convergent hydrogen bonds and another pair of nearly parallel hydrogen bonds.

Introduction

The structure and action of biomolecules critically depend upon non-covalent interactions. One feasible approach for elucidating the atomic details of these interactions is through the preparation and X-ray analysis of crystalline complexes involving the components of biopolymers and other small biomolecules. With this approach in view, we have already analysed the crystalline complexes between some amino acids (Bhat & Vijayan, 1976, 1977, 1978). Here we report the crystal structure of a 1:1 complex between the amino acid arginine and the vitamin ascorbic acid. It may be mentioned that this is the first crystalline complex between an amino acid on the one hand and a vitamin or a coenzyme on the other to be successfully analysed by X-ray methods.

Experimental

The crystals of the complex were grown by slow evaporation, in nitrogen atmosphere, of an aqueous solution of the components in molar proportion. The space group and the unit-cell dimensions were determined from X-ray diffraction photographs and the density was measured by flotation in a mixture of benzene and carbon tetrachloride.

Crystal data

L-Arginine L-ascorbate, $C_6H_{15}N_4O_2^+.C_6H_7O_6^-$; monoclinic, $P2_1$; $a = 5{\cdot}060\ (8)$, $b = 9{\cdot}977\ (9)$, $c = 15{\cdot}330\ (13)$ Å; $\beta = 97{\cdot}5\ (2)°$; $D_m = 1{\cdot}509\ (8)$, $D_c = 1{\cdot}516$ Mg m^{-3}; $Z = 2$; μ(Cu $K\alpha$) = 1·11 mm^{-1}.

The X-ray data were collected using the multiple-film equi-inclination technique (Cu $K\alpha$ radiation) and the intensities were estimated visually. The cylindrical specimen used for data collection had a mean radius of 0·4 mm and the photographs were recorded for reciprocal level Hkl, $H = 0$ through 4. The data were corrected for Lorentz–polarization factors, spot shape and absorption ($\mu r = 0{\cdot}44$). Of the 1860 independent reflections in the copper sphere, 1551 were recorded of which 1501 were in the measurable range.

The structure was solved by the non-centrosymmetric symbolic addition procedure (Karle & Karle, 1966) and refined using the full-matrix structure-factor least-squares program *LALS*, originally written by Gantzel, Sparks and Trueblood and modified by T. N. Bhat for the IBM 360/44 system with 128 K bytes memory. In the final cycles, anisotropic and isotropic temperature factors were used for non-hydrogen and hydrogen atoms, respectively. The refinement was terminated at $R = 0{\cdot}067$ for 1501 observed reflections. In the final cycle all the shifts, except that for the isotropic temperature factor of the hydrogen atom attached to O(15), were much smaller than the corresponding standard deviations. This temperature factor tended to increase abnormally though a difference Fourier map and geometrical considerations indicated the position of the hydrogen atom to be essentially correct. This hydrogen atom has a large thermal-vibration amplitude, presumably because it occurs in a flexible region of the molecule; as will be seen later, it is not involved in strong hydrogen-bonding, unlike the other hydroxyl hydrogen atoms in the structure. The temperature factor, however, was fixed at a reasonable value. The weighting function used in the final cycles had the form $1/(a + bF_o + cF_o^2)$, where $a = 0{\cdot}480$, $b = 0{\cdot}196$ and $c = -0{\cdot}001$. The form factors of the non-hydrogen atoms and the hydrogen atoms were taken from Cromer & Waber (1965) and Stewart, Davidson & Simpson (1965), respectively. The final positional parameters are given in Table 1.* The bond lengths and valency angles involving non-hydrogen atoms are shown in Fig. 1.

Discussion

The arginine molecule

The arginine molecule in the structure is a positively charged zwitterion in which the amino and the guanidyl groups are protonated and the carboxyl group is deprotonated. The bond lengths and angles in the molecule

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34789 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional parameters of non-hydrogen atoms* ($\times 10^4$) *and hydrogen atoms* ($\times 10^3$)

Isotropic temperature factors are also listed. The B values of non-hydrogen atoms are the equivalent isotropic temperature factors calculated from anisotropic thermal parameters using Hamilton's (1959) formula. The estimated standard deviations are given in parentheses.

	x	y	z	B (Å^2)
C(1)	1869 (10)	6069 (5)	5274 (3)	1·0 (2)
O(1)	108 (8)	5838 (4)	5750 (2)	2·0 (1)
O(2)	2393 (8)	7203 (4)	4981 (2)	1·9 (2)
C(2)	3575 (10)	4918 (5)	4998 (3)	1·0 (2)
N(1)	2971 (10)	3638 (4)	5437 (3)	1·3 (2)
C(3)	3208 (10)	4722 (5)	4002 (3)	1·4 (2)
C(4)	345 (10)	4516 (5)	3591 (3)	1·4 (2)
C(5)	313 (11)	4245 (5)	2611 (3)	1·7 (2)
N(6)	−2255 (9)	3971 (4)	2130 (3)	1·7 (2)
C(7)	−3242 (10)	2755 (5)	1972 (3)	1·2 (2)
N(8)	−2106 (11)	1699 (5)	2389 (3)	2·8 (2)
N(9)	−5328 (9)	2594 (5)	1377 (3)	2·0 (2)
C(11)	−245 (9)	8130 (5)	2316 (3)	1·3 (2)
O(11)	−1795 (8)	7847 (4)	2832 (2)	2·1 (1)
C(12)	1935 (9)	9042 (5)	2385 (3)	1·2 (2)
O(12)	2883 (7)	9767 (5)	3113 (2)	2·2 (1)
C(13)	2965 (10)	9070 (5)	1606 (3)	1·1 (1)
O(13)	4865 (8)	9759 (4)	1366 (2)	2·0 (1)
C(14)	1578 (9)	7995 (5)	1037 (3)	1·1 (2)
O(14)	−500 (7)	7517 (4)	1517 (2)	1·5 (1)
C(15)	3365 (9)	6834 (4)	873 (3)	0·9 (2)
O(15)	4407 (7)	6231 (4)	1688 (2)	1·3 (1)
C(16)	1898 (11)	5777 (5)	309 (3)	1·4 (2)
O(16)	3484 (9)	4660 (4)	185 (2)	2·2 (1)
H(C2)	575 (15)	529 (8)	521 (4)	2 (2)
H1(C3)	415 (17)	553 (9)	367 (5)	4 (2)
H2(C3)	440 (13)	382 (7)	381 (4)	1 (1)
H1(C4)	−52 (13)	385 (7)	392 (4)	1 (1)
H2(C4)	−76 (14)	536 (7)	371 (4)	2 (1)
H1(C5)	165 (13)	361 (7)	260 (4)	1 (1)
H2(C5)	133 (14)	519 (8)	237 (5)	2 (2)
H(N6)	−317 (18)	459 (11)	181 (6)	6 (2)
H1(N1)	132 (16)	352 (8)	523 (5)	1 (2)
H2(N1)	425 (14)	305 (7)	526 (4)	2 (1)
H3(N1)	325 (14)	382 (8)	603 (5)	3 (1)
H1(N8)	−73 (12)	176 (7)	287 (4)	1 (1)
H2(N8)	−312 (15)	105 (9)	223 (5)	2 (2)
H1(N9)	−616 (19)	298 (10)	97 (6)	6 (2)
H2(N9)	−581 (18)	141 (10)	123 (5)	5 (2)
H(O12)	155 (11)	1002 (5)	351 (3)	1 (1)
H(O15)	594 (20)	691 (11)	200 (6)	10 (2)
H(O16)	379 (18)	459 (11)	−14 (6)	6 (2)
H(C14)	93 (14)	823 (8)	39 (5)	2 (1)
H(C15)	497 (13)	709 (7)	66 (4)	1 (1)
H1(C16)	13 (15)	545 (9)	60 (5)	3 (2)
H2(C16)	122 (12)	617 (7)	−25 (4)	1 (1)

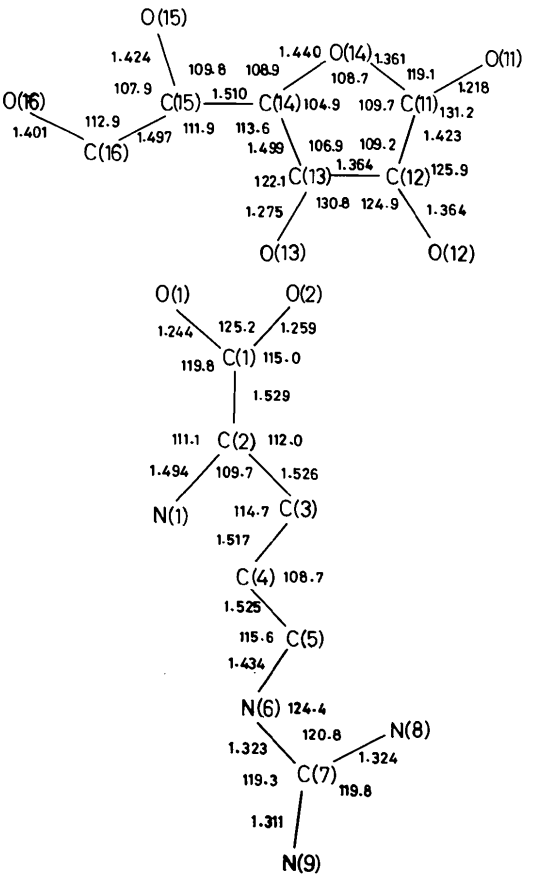


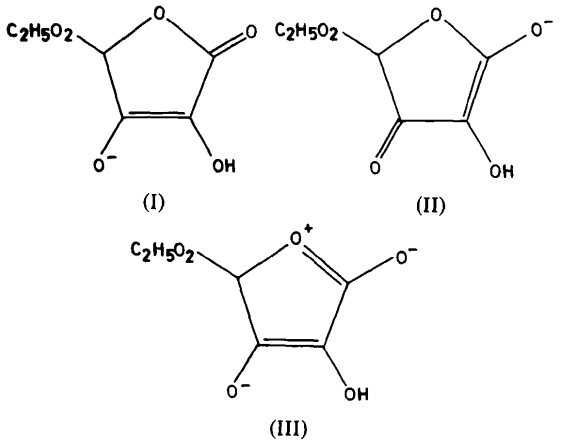
Fig. 1. Bond lengths (Å) and valency angles (°) involving non-hydrogen atoms. The estimated standard deviations in bond lengths and angles are 0·006 Å and 0·4°, respectively.

are similar to those found in other crystal structures containing arginine (Vijayan, 1976). The conformation of the molecule is defined by the following torsional angles (IUPAC–IUB Commission on Biochemical Nomenclature, 1970): $\psi^1 = -5$, $\psi^2 = 175$, $\chi^1 = 69$, $\chi^2 = -176$, $\chi^3 = 177$, $\chi^4 = -94$, $\chi^{51} = 12$, $\chi^{52} = -166°$. The side chain of arginine can assume a number of different conformations on account of its length and flexibility. As pointed out by Bhat & Vijayan (1977), eight independent side-chain conformations have so far been observed in the crystal structures of arginine, its salts and complexes. The conformation observed in the present structure is different from all of them and, hence, represents the ninth unique conformation observed in crystal structures.

The ascorbate anion

The ionization of the ascorbic acid molecule in the structure takes place by the deprotonation of O(13) as in the case of its metal complexes (Hvoslef, 1969; Hvoslef & Kjellevold, 1974; Hughes, 1973; McClelland, 1974). However, the present structure provides the first description of the ascorbate anion unaffected by the geometrical constraints and disturbances imposed by the requirements of metal coordination. The bond lengths and angles in the anion are comparable to those observed in the metal complexes. The distribution of bond lengths indicates some degree of electron delocalization in the fragment of the anion O(14),

C(11), O(11), C(12), O(12), C(13) and O(13). The anion can, in fact, be considered as a resonance hybrid of (I), (II) and (III). The fact that the C(11)–C(12) and the C(13)–O(13) bonds are considerably longer than the C(12)–C(13) and the C(11)–O(11) bonds, respectively, indicates the preponderence of (I). The bulk of the negative charge is hence situated on O(13). The contribution of form (III) explains, in fact, the unequal lengths of C(14)–O(14) and C(11)–O(14), a feature observed in structures containing the lactone group.



For the purpose of overall geometrical description, the ascorbate anion can be considered as made up of two parts, namely, the side chain consisting of C(15), O(15), C(16) and O(16), and the remaining roughly planar fragment consisting of the five-membered ring and the attached oxygen atoms. The latter contains a lactone group [C(14), O(14), C(11), O(11), C(12)] and a deprotonated enediol group [C(12), O(12), C(13), O(13)]. In the present structure, both the groups are planar within experimental error. Small, though significant ($\Delta > 3\sigma$), deviations from planarity have been observed in these groups in the metal complexes. It is felt that these deviations are likely to have been caused by packing forces, especially those arising from metal coordination. In the metal complexes, the angle between the mean planes of the two groups varies between 1 and 8°. In the present structure this angle is 5°.

The torsional angles that define the conformation of the side chain are illustrated in Fig. 2. The orientation of the side chain with respect to the planar moiety is governed by a rotation about the C(14)–C(15) single bond. Among the three possible staggered conformations, the one in which O(15) is staggered between O(14) and C(13) does not involve any steric contact between two carbon atoms. The ascorbate ion in the present structure has this conformation. The same conformation is observed in the crystal structures of ascorbic acid and its metal complexes except calcium ascorbate. In calcium ascorbate (Hvoslef & Kjellevold, 1974), one of the two crystallographically independent

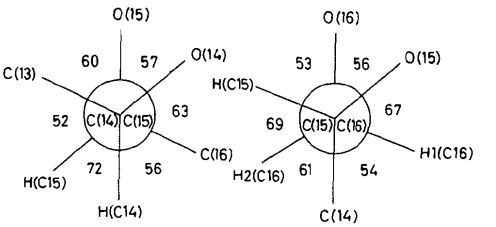


Fig. 2. Torsional angles (°) about C(14)–C(15) and C(15)–C(16) in the side chain of the ascorbate anion.

molecules has a conformation in which C(16) is staggered between O(14) and C(13). In the other ascorbate anion, the hydrogen atom attached to C(14) is staggered between O(14) and C(13). Both these conformations involve a steric contact between the carbon atoms C(16) and C(13).

The second torsional angle necessary to define the conformation of the side chain corresponds to a rotation about the C(15)–C(16) bond. O(16) could be staggered between C(14) and H(C15), O(15) and H(C15) or C(14) and O(15). When the conformation about the C(14)–C(15) bond is such that O(15) is staggered between C(13) and O(14) (as in the present structure as well as in all metal complexes except one), it can be readily seen from an examination of a molecular model that a conformation about the C(15)–C(16) bond with O(16) staggered between C(14) and O(15) leads to steric contacts of O(16) with C(14) and O(15) as well as O(14). Therefore, from steric considerations the favourable conformations are those in which O(16) is staggered either between C(14) and H(C15) or between O(15) and H(C15). Indeed, in ascorbic acid and all its metal complexes [except calcium ascorbate in which the conformation about the C(14)–C(15) bond is different], O(16) takes up one or the other of these two positions. In the present structure O(16) is staggered between O(15) and H(C15).

Crystal structure and intermolecular interactions

The crystal structure of arginine ascorbate is shown in Fig. 3. The hydrogen-bond parameters are given in Table 2. All the hydrogen atoms attached to nitrogen and oxygen atoms take part in hydrogen bonding. Of these, H3(N1) and H(O15) are involved in bifurcated hydrogen bonds. Judging by the O···O distances, the bifurcated hydrogen bond involving H(O15) appears to be rather weak. Each hydroxyl group in the ascorbate ion takes part in two hydrogen bonds, one as an acceptor and the other as a donor. The two carbonyl oxygens in the ascorbate ion and the two carboxylate oxygens in the arginine molecule accept at least two hydrogen bonds each. The deprotonated oxygen atom O(13) in the ascorbate ion, in fact, accepts three hydrogen bonds.

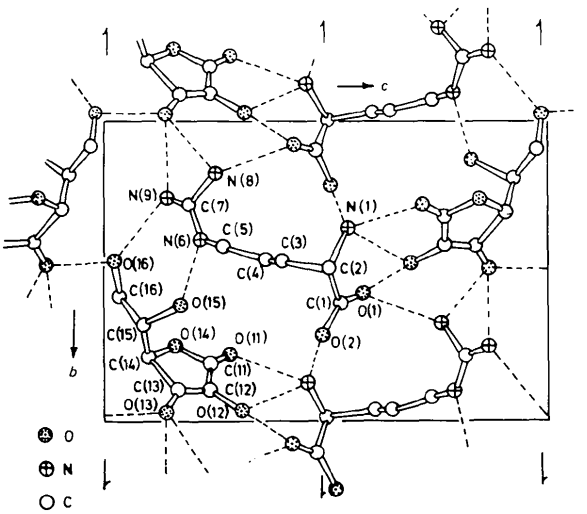


Fig. 3. Crystal structure of arginine ascorbate as viewed along the *a* axis. Broken lines indicate hydrogen bonds. For clarity, the bifurcated hydrogen bond between O(15) and both O(11) and O(14) in the molecule related by an *a* translation is not shown.

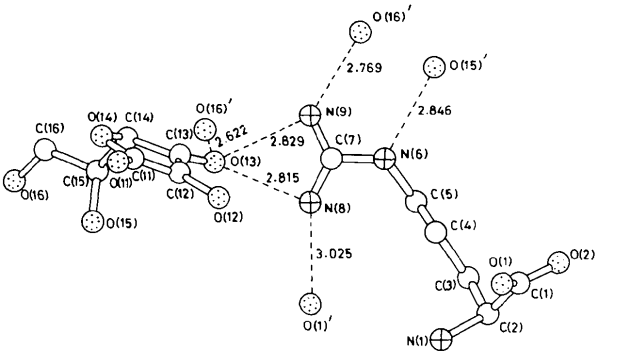


Fig. 4. The specific ion-pair interaction between the guanidyl group and the ascorbate ion. The primed atoms belong to the neighbouring molecules.

Table 2. *Hydrogen-bond parameters*

A–H···*B*	*A*···*B* (Å)	∠H–*A*···*B* (°)
N(1)–H1(N1)···O(2)$^{(e)}$	3·061 (6)	22 (5)
N(1)–H2(N1)···O(2)$^{(g)}$	2·891 (6)	10 (4)
N(1)–H3(N1)···O(11)$^{(e)}$	2·904 (6)	34 (5)
N(1)–H3(N1)···O(12)$^{(g)}$	3·065 (5)	37 (5)
N(6)–H(N6)···O(15)$^{(a)}$	2·846 (6)	20 (6)
N(8)–H1(N8)···O(1)$^{(e)}$	3·025 (6)	33 (4)
N(8)–H2(N8)···O(13)$^{(b)}$	2·815 (6)	17 (5)
N(9)–H1(N9)···O(16)$^{(a)}$	2·769 (6)	23 (7)
N(9)–H2(N9)···O(13)$^{(b)}$	2·830 (6)	16 (6)
O(12)–H(O12)···O(1)$^{(d)}$	2·676 (6)	11 (3)
O(15)–H(O15)···O(11)$^{(c)}$	2·913 (5)	11 (5)
O(15)–H(O15)···O(14)$^{(c)}$	2·921 (5)	36 (5)
O(16)–H(O16)···O(13)$^{(f)}$	2·622 (5)	10 (9)

Symmetry code

(*a*) $x-1, y, z$
(*b*) $x-1, y-1, z$
(*c*) $x+1, y, z$
(*d*) $-x, \frac{1}{2}+y, -z+1$
(*e*) $-x, \frac{1}{2}+y-1, -z+1$
(*f*) $-x+1, \frac{1}{2}+y-1, -z$
(*g*) $-x+1, \frac{1}{2}+y-1, -z+1$

As in the cases of lysine aspartate, arginine glutamate and histidine–aspartic acid (Bhat & Vijayan, 1976, 1977, 1978), the unlike molecules aggregate separately into alternating layers in the crystal. The molecules in the arginine layer, parallel to the *ab* plane and centred on $c = \frac{1}{2}$, are held together by interactions involving α-amino and α-carboxylate groups so that the side chains are free to take part in other intermolecular interactions, a situation analogous to that found in proteins. The arrangement of arginine molecules in the structure, like that in arginine glutamate, in fact, appears to be somewhat similar to an extended peptide chain with the side chains sticking out alternately on opposite sides of the main chain. The pleated layer of ascorbate anions is also parallel to the *ab* plane, but centred on $c = 0$. The two layers of unlike molecules are held together principally through the interactions involving the side-chain guanidyl group of arginine with ascorbate ions, a situation analogous to what might exist in the binding of ascorbate ions to proteins. In particular, there exists a specific ion-pair interaction between the guanidyl group and the deprotonated oxygen atom O(13), which carries the bulk of the negative charge, in the ascorbate ion. This interaction, which involves electrostatic attraction as well as two N–H···O hydrogen bonds with the oxygen atom as the common acceptor, is illustrated in Fig. 4. As can be seen from Figs. 3 and 4, yet another interesting interaction, which involves two nearly parallel N–H···O hydrogen bonds, is between O(15) and O(16) of the side chain of an ascorbate ion on the one hand, and N(6) and N(9) of the guanidyl group on the other.

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X-ray Studies on Crystalline Complexes Involving Amino Acids. V. The Structure of L-Serine–L-Ascorbic Acid*

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Abstract

L-Serine–L-ascorbic acid, $C_3H_7NO_3.C_6H_8O_6$, a 1:1 complex between the amino acid serine and the vitamin ascorbic acid, crystallizes in the orthorhombic space group $P2_12_12_1$ with four formula units in a cell of dimensions a = 5·335 (3), b = 8·769 (2), c = 25·782 (5) Å. The structure was solved by direct methods and refined by full-matrix least squares to an R of 0·036 for 951 observed reflections. Both molecules are neutral in the structure. The conformation of the serine molecule is different from that observed in the crystal structures of L-serine, DL-serine and L-serine monohydrate. The enediol group in the ascorbic acid molecule is planar, whereas significant departures from planarity are observed in the lactone group. The conformation of this molecule is similar to that observed in arginine ascorbate. The unlike molecules aggregate into separate columns in the crystal structure. The columns are held together by hydrogen bonds. Among these, a pair of hydrogen bonds between the enediol group of ascorbic acid and the carboxylate group of serine provides a possible model for a specific interaction between ascorbic acid and a carboxylate ion.

Introduction

As part of a programme of X-ray studies on crystalline complexes involving amino acids, among themselves and with other biomolecules, we report the crystal structure of a 1:1 complex between the amino acid serine and the vitamin ascorbic acid. The crystal structure of another such complex, that between arginine and ascorbic acid, has already been reported (Sudhakar & Vijayan, 1980). Both of the molecules in arginine ascorbate are ionized and the complex is stabilized primarily through the interactions between the ascorbate anion and the positively charged guanidyl group of arginine. The side chain of serine is not easily ionizable and, hence, it was thought likely that the ascorbic acid would remain neutral in its complex with serine. Therefore, the X-ray analysis of this complex was undertaken in order to study, at the atomic resolution, the possible non-covalent interaction between neutral ascorbic acid and an amino acid.

Experimental

Transparent, plate-like crystals of the complex were grown from an aqueous solution of the components in molar proportion by slow evaporation in a nitrogen atmosphere. The unit-cell dimensions and the space group were determined from X-ray diffraction photographs. The former were subsequently refined on a four-circle diffractometer. The density was measured by flotation in a mixture of chloroform and carbon tetrachloride.

Crystal data

L-Serine–L-ascorbic acid, $C_3H_7NO_3.C_6H_8O_6$; orthorhombic, $P2_12_12_1$; a = 5·335 (3), b = 8·769 (2), c = 25·782 (5) Å; D_m = 1·56 (1), D_c = 1·55 Mg m^{-3}; Z = 4; μ(Mo $K\alpha$) = 0·1524 mm^{-1}.

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