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Changes in Conformation and Bonding of Ascorbic Acid by Ionization. The Crystal Structure of Sodium Ascorbate

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The crystal structure of sodium ascorbate, $C_6H_7O_6Na$, has been determined and the parameters refined to an R index of 5·8% for the 854 observed X-ray reflexions. The space group is $P2_12_12_1$ with $a=19{\cdot}051$, $b=4{\cdot}490$, $c=8{\cdot}516$ Å and with four molecules in the unit cell. The sodium ion is surrounded by six oxygen atoms forming a distorted octahedron where the Na–O distances vary between 2·416 and 2·725 Å. Bonding and conformational changes from those in ascorbic acid have been observed, and the anion may be regarded as a mesomer between two structural formulae. The hydrogen atoms are located, and the H atom attached to O(3) is proved to be the protolytic one.

Introduction

Comprehensive studies of ascorbic acid have provided empirical rules for the atomic arrangements necessary for the antiscorbutic effect. The presence of a furan ring which includes an enediol group next to a carbonyl group is imperative, and this configuration is also reponsible for the acidity and reducing power of the substance. Moreover, the proper configuration at the asymmetric carbon atom C(4) and a side chain of at least two carbon atoms is necessary for the biological effect. Other details in the molecule are of somewhat less importance. A survey of the chemistry of ascorbic acid is given in *Ascorbinsäure* (1965).

The first oxidation product of Vitamin C, the dehydroascorbic acid $C_6H_6O_6$ has the same effect *in vivo* as the vitamin itself, presumably because of the reversible equilibrium between the two substances. The structural formula of the dehydro compound is not known with certainty, but we hope to solve the problem by means of an X-ray investigation.

We consider it in any case to be of interest to see what happens to the ascorbic acid molecule when it gives off hydrogen – either by ionization or by oxidation. Since the oxidation of the acid proceeds more easily in an alkaline than in an acid medium, the formation of an ascorbate anion might be the first step in this process.

The structure of ascorbic acid itself is known from X-ray and neutron diffraction analyses (Hvoslef, 1968 *a*, *b*), and this enables us to study the changes that occur in each step.

We also wished to test Euler & Eistert's (1957) proposal that the hydrogen atom attached to O(3) is the most likely one to leave the molecule on ionization. Salts of the bivalent anion are not known.

The sodium salt seemed to be a convenient choice, since the cation is light enough to permit a reasonably accurate determination of the hydrogen positions. Moreover, no water of crystallization is present in this compound.

Experimental

Crystals of sodium ascorbate were grown from aqueous solution, and a specimen of approximately spherical shape was picked out. The radius was 0·015 cm, and the linear absorption coefficient for Cu $K\alpha$ radiation was 19·4 cm^{-1}. For this crystal the variation of the transmission over the angular range was small, and no correction for absorption was considered to be necessary.

X-ray intensities were collected on an integrating Weissenberg camera with Ni-filtered Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å). The four layers recorded by rotation about **b** and the five layers recorded by rotation about **c** were measured photometrically. Copper radiation allows a maximum of 944 unique reflexions to be recorded for this unit cell, and 854 were strong enough to be measured. The non-observed reflexions were included in the calculations by taking one-third of the minimum observable intensity, except for the centrosymmetric projections, where one-quarter was used (Hamilton, 1955).

The axial lengths were determined by means of Guinier photographs, and the experimental density was found to be 1·79 $g.cm^{-3}$.

Unit cell and space group

$a=19{\cdot}051(9)$ Å	$C_6H_7O_6Na$
$b=\ 4{\cdot}490(2)$	$M=198{\cdot}108$
$c=\ 8{\cdot}516(4)$	$V=728{\cdot}45$ Å^3
Space group $P2_12_12_1$	$d_{calc}=1{\cdot}7994$ $g.cm^{-3}$
$Z=4$	

Structure determination

The obvious way of attacking the present structural problem was to solve the [010] projection. The short b axis of 4·490 Å seemed likely to show a well resolved ring system, identifiable at an early stage. We also expected intramolecular Patterson vectors similar to those in ascorbic acid. If this were the case it might help to find the orientation of the anion and thus facilitate the solution of the whole structural problem. The Patterson projection was, however, difficult to interpret, and this method of approach was therefore abandoned.

Since the sodium atom was too light for the determination of the signs of the structure factors, the phases were found by direct methods. No conclusions could be drawn from the Harker–Kasper inequalities because of the small values of the unitary structure factors, and Grison's (1951) criteria for the use of Sayre's equations also failed to give any definite information. Nevertheless, 54 signs were determined by the use of computer versions of the methods described by Zachariasen (1952) and Woolfson (1961).

In the electron density map based upon the 54 signs, six false peaks led to some confusion, but as soon as the true peaks were identified the refinement gave a conventional R index of 9% for the $h0l$ reflexions.

The [001] zone was analysed in the same manner, and although the **c** projection suffers from overlap, 28 correct and 4 wrong signs were determined. Subsequent refinement gave an R index of 13% for this zone.

Refinement of the structure

The different layers were put on approximately the same scale by means of common reflexions obtained by

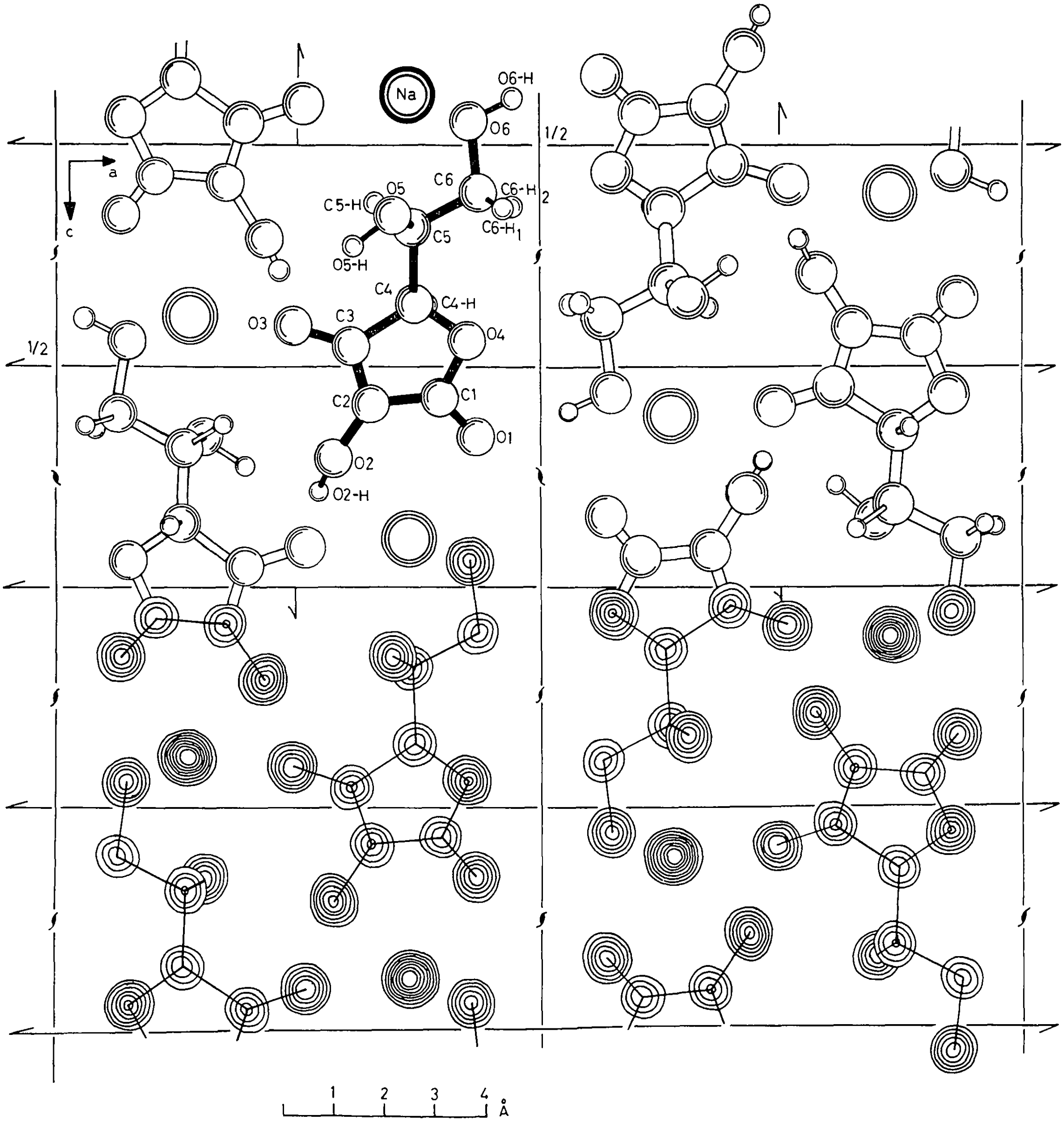


Fig. 1. View of the structure of sodium ascorbate along [010] and the corresponding composite three-dimensional electron density projection. Contours at intervals of 2·5 e.Å^{-3}, starting at 5 e.Å^{-3}. The reference formula unit is indicated by solid lines.

rotation about the b and c axes. The absolute values of the structure factors were established by comparison with the calculated values in the solved projections.

Least-squares programs in block-diagonal and full-matrix versions were used in the refinement of the parameters. The latter version was used in the final stage only. The function to be minimized was

$$\sum_{hkl} w_{hkl}^2 \left(|F_{\text{obs}}| - G|F_{\text{calc}}|\right)^2 ,$$

where w_{hkl} is the weight function and G is the reciprocal scale factor. The following weight scheme was used: for F_{obs} less than 5·0, $w = 8{\cdot}0$, and for larger values $w = 17{\cdot}88(F_{\text{obs}})^{-1/2}$.

The 'heavy' atoms were first refined with isotropic temperature parameters, and the interlayer scale factors were checked from time to time. When the conventional R index had reached a value of 10%, a difference Fourier synthesis was calculated in the hope of getting information about the hydrogen atoms. These were readily found, and from this stage they were included in the refinement process. In addition, the analysis of the other atoms was extended to include anisotropic thermal vibrations. Further refinements and interlayer scaling adjustments gradually lowered the R index to 6·75% by use of the block-diagonal least-squares program. A direct Fourier synthesis and a view of the structure is shown in Fig. 1. Again a difference Fourier synthesis was calculated in order to locate the hydrogen atoms, and the result is shown in Fig. 2.

We now proceeded to correct the observed structure factors for secondary extinction effects, with the use of a computer version of Zachariasen's (1963) formula. The extinction coefficient C was found to be $2{\cdot}9 \times 10^{-5}$ in this case.

Subsequent full-matrix least-squares refinements were terminated when no further shifts occurred at an R index of 5·8% for the observed reflexions. The

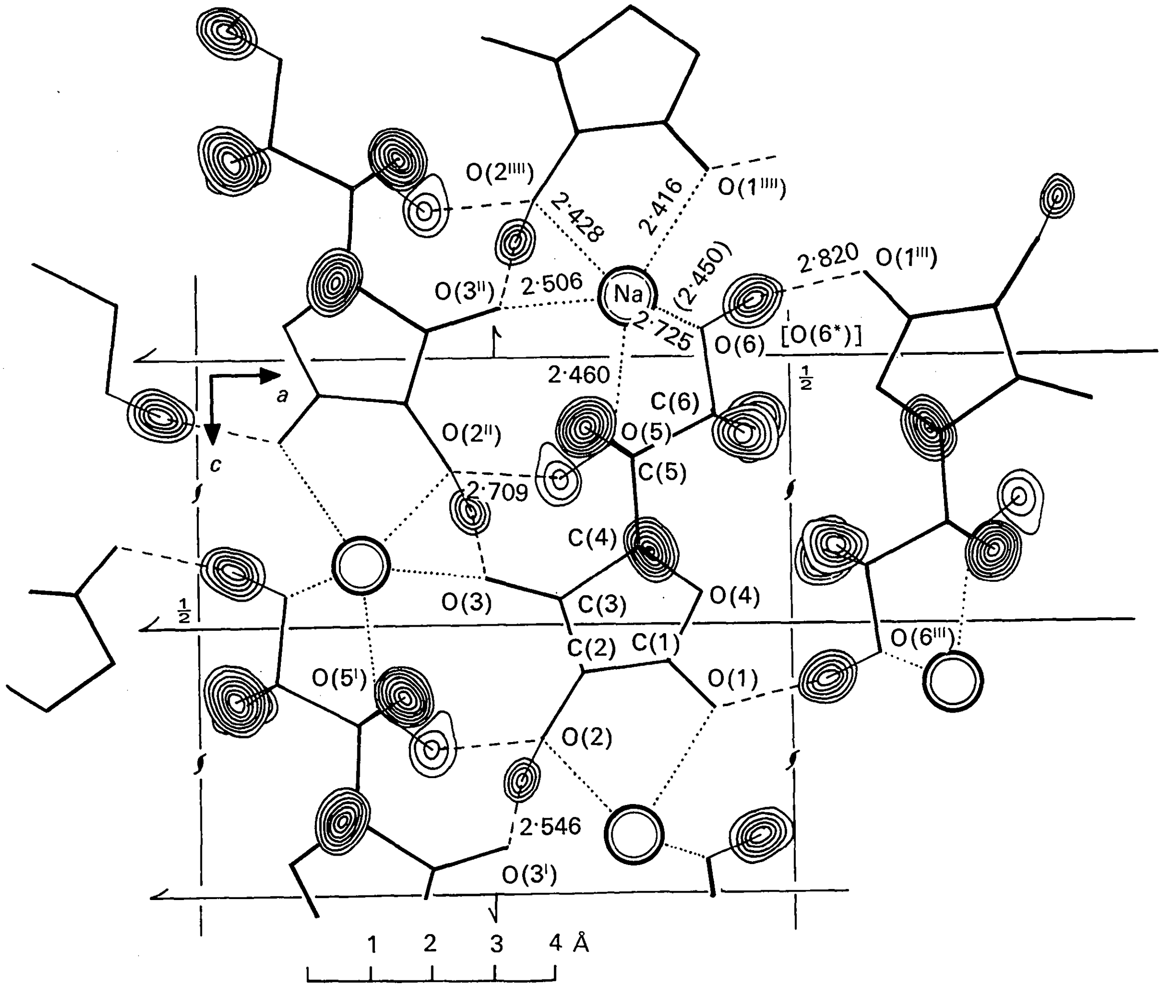


Fig. 2. Composite three-dimensional difference electron density map showing the hydrogen atoms as seen along [010]. Contours at intervals of 0·1 e.Å^{-3}, starting at 0·3 e.Å^{-3}. Broken lines indicate hydrogen bonds, and dotted lines indicate sodium–oxygen interactions.

R index for all 944 reflexions was 6·5%. The corresponding atomic parameters and their standard deviations are given in Table 1, the thermal parameters in Table 2 and the observed and calculated structure factors in Table 3.

Table 1. *Fractional coordinates, x,y,z, of atoms in the asymmetric unit of the sodium ascorbate unit cell*

Standard deviations in parentheses. The hydrogen atoms are identified by the C or O atoms to which they are attached.

	x	*y*	*z*
Na⁺	0·3644 (1)	0·3630 (5)	−0·1129 (2)
O(1)	0·4331 (2)	0·4869 (9)	0·6578 (4)
O(2)	0·2854 (1)	0·6297 (8)	0·7132 (4)
O(3)	0·2425 (2)	0·9593 (8)	0·4095 (4)
O(4)	0·4243 (2)	0·7601 (9)	0·4273 (4)
O(5)	0·3485 (2)	0·5441 (7)	0·1574 (4)
O(6)	0·4272 (2)	0·8983 (10)	−0·0581 (4)
C(1)	0·3968 (2)	0·6430 (11)	0·5708 (5)
C(2)	0·3251 (2)	0·7217 (10)	0·5860 (5)
C(3)	0·3035 (2)	0·8682 (10)	0·4530 (5)
C(4)	0·3696 (2)	0·9276 (11)	0·3588 (5)
C(5)	0·3667 (2)	0·8441 (10)	0·1840 (5)
C(6)	0·4364 (2)	0·9037 (11)	0·1076 (5)
O(2)–H	0·270 (4)	0·737 (20)	0·785 (10)
O(5)–H	0·308 (5)	0·511 (25)	0·194 (12)
O(6)–H	0·464 (5)	0·884 (25)	−0·104 (11)
C(4)–H	0·385 (3)	1·172 (13)	0·365 (6)
C(5)–H	0·333 (2)	0·979 (12)	0·137 (6)
C(6)–H(1)	0·459 (4)	1·121 (18)	0·139 (9)
C(6)–H(2)	0·467 (3)	0·741 (14)	0·141 (7)

Table 2. *Thermal parameters, b_{ij}, of the atoms in the asymmetric unit of the sodium ascorbate unit cell*

Standard deviations in parentheses. All b_{ij} values are multiplied by 10^4. The hydrogen atoms are identified by the C or O atoms to which they are attached, and only their isotropic *B* values are given.

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Na⁺	15 (1)	237 (10)	44 (2)	13 (4)	5 (2)	46 (10)
O(1)	10 (1)	294 (19)	45 (4)	50 (7)	4 (3)	77 (17)
O(2)	7 (1)	172 (15)	41 (4)	−5 (6)	11 (3)	32 (15)
O(3)	8 (1)	233 (17)	40 (4)	18 (6)	2 (3)	26 (17)
O(4)	5 (1)	341 (20)	41 (4)	28 (7)	2 (3)	92 (18)
O(5)	11 (1)	88 (14)	55 (4)	−10 (6)	15 (3)	−20 (16)
O(6)	9 (1)	399 (22)	31 (4)	−6 (8)	11 (3)	37 (18)
C(1)	9 (1)	222 (24)	31 (5)	9 (9)	2 (4)	−13 (22)
C(2)	10 (1)	145 (19)	36 (5)	27 (8)	12 (4)	35 (21)
C(3)	8 (1)	66 (17)	39 (5)	−4 (7)	4 (3)	−22 (18)
C(4)	8 (1)	204 (21)	37 (5)	33 (8)	−7 (4)	32 (21)
C(5)	8 (1)	108 (19)	40 (5)	−27 (8)	−2 (4)	62 (19)
C(6)	9 (1)	181 (20)	37 (5)	−2 (8)	−7 (4)	43 (20)
O(2)–H	3·8 (1·7)					
O(5)–H	5·2 (2·2)					
O(6)–H	5·0 (2·2)					
C(4)–H	0·5 (1·0)					
C(5)–H	−0·2 (0·8)					
C(6)–H(1)	2·5 (1·6)					
C(6)–H(2)	0·5 (1·0)					

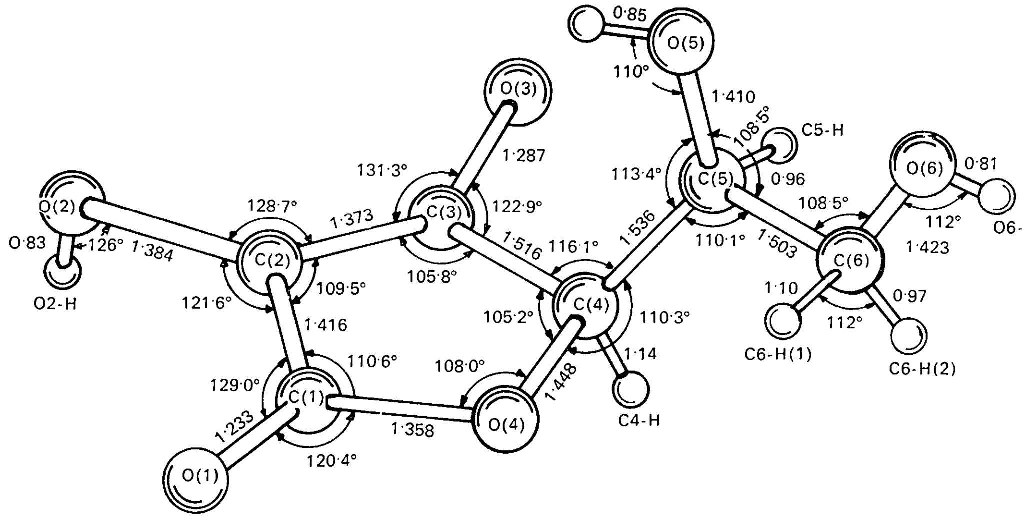


Fig. 3. Some bonding distances and angles in the ascorbate anion.

Table 3. *Observed and calculated structure factors*

*F*obs are corrected for secondary extinction effects, and the zero observed reflexions (indicated by ×) are included by taking one-third of the minimum observable intensities, except for the centrosymmetric projections, where one-quarter was taken.

h	k	l	F_{obs}	$\|F_{calc}\|$
0	0	2	28.9	28.7
0	0	4	78.3	87.1
0	0	6	26.1	26.3
0	0	8	16.7	17.1
0	0	10	3.4	3.8
0	1	1	67.1	62.5
0	1	2	76.1	74.4
0	1	3	7.3	7.3
0	1	4	2.9	1.8
0	1	5	26.7	27.7
0	1	6	22.0	22.2
0	1	7	20.2	19.8
0	1	8	14.2	15.5
0	1	9	6.7	6.7
0	1	10	10.9	11.4
0	2	0	27.7	24.2
0	2	1	23.2	21.5
0	2	2	19.1	18.2
0	2	3	12.3	11.9
0	2	4	23.9	22.2
0	2	5	17.6	18.3
0	2	6	19.5	19.6
0	2	7	10.3	9.9
0	2	8	9.5	8.4
0	2	9	12.6	11.1
0	2	10	5.7	5.2
0	3	1	7.0	7.7
0	3	2	26.9	28.9
0	3	3	6.9	5.5
0	3	4	20.1	20.6
0	3	5	2.2 x	2.0
0	3	6	27.3	26.9
0	3	7	2.2 x	2.7
0	3	8	6.1	4.5
0	3	9	9.3	10.3
0	4	0	22.5	21.4
0	4	1	7.2	5.0
0	4	2	3.0 x	1.2
0	4	3	4.3 x	3.7
0	4	4	3.0 x	1.4
0	4	5	6.2	5.0
0	5	1	7.9	6.3
0	5	2	7.0	6.8
0	5	3	3.7 x	4.1
0	5	4	2.3 x	2.5
0	5	5	1.6 x	1.6
1	0	1	2.5 x	3.2
1	0	2	6.5	6.8
1	0	3	16.5	15.5
1	0	4	63.7	67.5
1	0	5	11.6	11.3
1	0	6	14.7	15.3
1	0	7	10.2	8.9
1	0	8	2.3	1.2
1	0	9	4.7	4.8
1	0	10	7.2	7.7
1	1	0	0.9 x	1.7
1	1	1	30.4	28.4
1	1	2	45.0	43.9
1	1	3	28.2	28.2
1	1	4	19.3	18.2
1	1	5	17.0	16.7
1	1	6	22.2	22.1
1	1	7	12.4	12.7
1	1	8	13.2	13.3
1	1	9	10.6	11.0
1	1	10	3.0	2.7
1	2	0	49.1	44.8
1	2	1	15.2	15.6
1	2	2	13.7	13.4
1	2	3	18.9	17.4
1	2	4	26.7	26.7
1	2	5	8.7	8.8
1	2	6	4.7	4.2
1	2	7	17.8	18.7
1	2	8	16.8	14.8
1	2	9	14.1	13.0
1	2	10	3.2	3.4
1	3	0	10.7	12.1
1	3	1	17.1	18.3
1	3	2	10.8	10.9
1	3	3	24.9	23.7
1	3	4	9.3	8.5
1	3	5	15.1	14.7
1	3	6	21.0	21.6
1	3	7	14.0	13.5
1	3	8	11.6	11.3
1	3	9	4.3	4.1
1	4	0	4.3	3.5
1	4	1	16.7	15.8
1	4	2	10.9	10.6
1	4	3	22.2	19.4
1	4	4	7.7	8.6
1	4	5	10.8	11.1
1	5	0	5.7	4.5
1	5	1	6.8	5.6
1	5	2	11.6	9.7
1	5	3	3.7 x	5.0
1	5	4	2.3 x	3.4
1	5	5	1.6 x	2.9
2	0	0	26.5	27.4
2	0	1	3.6	4.0
2	0	2	23.1	23.4
2	0	3	30.8	32.1
2	0	4	9.4	8.4
2	0	5	11.1	11.1
2	0	6	8.7	9.1
2	0	7	14.9	14.4
2	0	8	1.3 x	1.9
2	0	9	13.8	14.3
2	0	10	10.9	11.4
2	1	0	89.8	88.2
2	1	1	58.7	57.0
2	1	2	30.9	29.0
2	1	3	25.4	26.3
2	1	4	10.6	10.3
2	1	5	15.2	14.4
2	1	6	10.4	8.8
2	1	7	14.1	14.2
2	1	8	30.6	31.1
2	1	9	6.7	7.1
2	1	10	8.7	8.5
2	2	0	9.2	7.4
2	2	1	35.5	33.1
2	2	2	52.5	52.0
2	2	3	14.7	12.9
2	2	4	26.5	26.1
2	2	5	19.7	19.6
2	2	6	9.0	8.9
2	2	7	17.5	17.0
2	2	8	4.6	3.3
2	2	9	4.8	5.1
2	2	10	2.8	3.4
2	3	0	12.9	13.3
2	3	1	35.5	36.3
2	3	2	8.7	7.7
2	3	3	18.8	18.7
2	3	4	10.7	10.1
2	3	5	4.1	5.6
2	3	6	13.9	12.8
2	3	7	12.7	10.8
2	3	8	4.9	3.3
2	3	9	5.9	6.4
2	4	0	8.5	7.1
2	4	1	15.0	14.7
2	4	2	8.6	7.7
2	4	3	11.0	9.7
2	4	4	17.2	15.9
2	4	5	12.4	13.1
2	5	0	8.1	7.8
2	5	1	3.9	3.5
2	5	2	2.7 x	3.8
2	5	3	3.6 x	1.6
2	5	4	17.9	14.9
2	5	5	9.6	7.6
3	0	1	7.4	8.1
3	0	2	16.4	16.9
3	0	3	20.6	21.3
3	0	4	18.1	17.6
3	0	5	22.7	21.8
3	0	6	17.1	15.5
3	0	7	35.9	37.0
3	0	8	4.6	4.7
3	0	9	14.3	14.6
3	0	10	9.9	10.5
3	1	0	16.9	14.8
3	1	1	58.8	57.6
3	1	2	49.5	48.6
3	1	3	27.1	26.1
3	1	4	24.7	24.8
3	1	5	20.0	19.5
3	1	6	2.8	4.2
3	1	7	19.8	19.9
3	1	8	14.2	13.6
3	1	9	2.7	3.4
3	1	10	3.6	3.6
3	2	0	10.5	10.5
3	2	1	57.5	55.7
3	2	2	38.7	37.3
3	2	3	20.0	18.7
3	2	4	17.9	17.4
3	2	5	32.7	32.5
3	2	6	5.2	5.2
3	2	7	11.1	11.7
3	2	8	6.5	7.1
3	2	9	3.8	3.3
3	2	10	5.7	5.6
3	3	0	21.0	21.4
3	3	1	7.5	7.6
3	3	2	14.7	15.4
3	3	3	25.3	22.7
3	3	4	12.1	11.9
3	3	5	33.1	29.9
3	3	6	8.4	7.1
3	3	7	8.9	8.6
3	3	8	7.7	6.4
3	3	9	8.4	10.1
3	4	0	8.5	8.8
3	4	1	10.2	9.5
3	4	2	7.7	8.6
3	4	3	11.0	9.1
3	4	4	12.1	12.8
3	4	5	9.8	11.5
3	5	0	10.6	9.2
3	5	1	10.2	9.4
3	5	2	2.7 x	4.1
3	5	3	3.6 x	6.7
3	5	4	7.1	6.9
3	5	5	9.9	8.6
4	0	0	70.6	86.3
4	0	1	9.9	10.3
4	0	2	6.4	5.9
4	0	3	31.8	31.6
4	0	4	45.9	47.9
4	0	5	1.9	1.7
4	0	6	9.5	10.3
4	0	7	21.4	21.0
4	0	8	3.3	3.2
4	0	9	11.7	11.4
4	0	10	6.9	7.1
4	1	0	9.3	9.1
4	1	1	27.6	26.8
4	1	2	35.3	33.3
4	1	3	7.7	6.3
4	1	4	15.4	15.8
4	1	5	44.4	45.4
4	1	6	12.4	12.5
4	1	7	4.3	4.2
4	1	8	20.4	21.8
4	1	9	6.5	6.1
4	1	10	4.5	4.9
4	2	0	9.2	9.0
4	2	1	21.0	20.4
4	2	2	26.7	25.7
4	2	3	31.2	30.9
4	2	4	15.0	12.4
4	2	5	5.3	4.2
4	2	6	18.9	19.4
4	2	7	18.8	19.0
4	2	8	6.8	7.5
4	2	9	1.9	1.5
4	2	10	10.5	13.1
4	3	0	4.5	3.2
4	3	1	25.5	26.9
4	3	2	20.6	20.8
4	3	3	4.8	5.3
4	3	4	23.6	21.8
4	3	5	9.2	8.2
4	3	6	15.7	13.3
4	3	7	13.1	11.1
4	3	8	5.8	5.1
4	3	9	3.8	4.2
4	4	0	14.2	12.7
4	4	1	16.7	17.9
4	4	2	6.6	7.2
4	4	3	7.7	5.7
4	4	4	15.2	14.6
4	4	5	6.1	5.9
4	5	0	2.1 x	.9
4	5	1	7.5	8.6
4	5	2	2.6 x	1.9
4	5	3	3.5 x	2.3
4	5	4	8.9	9.6
4	5	5	12.5	12.4
5	0	1	18.9	18.4
5	0	2	6.5	5.8
5	0	3	28.8	28.3
5	0	4	33.4	30.7
5	0	5	4.3	2.9
5	0	6	33.7	33.6
5	0	7	5.7	5.8
5	0	8	1.3 x	1.2
5	0	9	8.5	8.2
5	0	10	24.7	23.6
5	1	0	47.0	46.8
5	1	1	31.4	31.2
5	1	2	37.6	35.6
5	1	3	19.8	17.8
5	1	4	25.4	25.5
5	1	5	17.1	16.5
5	1	6	29.2	28.4
5	1	7	4.3	4.8
5	1	8	4.2	5.3
5	1	9	18.1	16.4
5	1	10	8.1	7.3
5	2	0	39.3	36.7
5	2	1	14.8	13.9
5	2	2	20.9	19.7
5	2	3	10.3	9.6
5	2	4	12.0	11.1
5	2	5	15.5	14.1
5	2	6	3.4	3.5
5	2	7	5.4	5.4
5	2	8	5.9	6.2
5	2	9	8.4	8.1
5	2	10	6.6	8.2
5	3	0	7.6	6.5
5	3	1	21.7	21.2
5	3	2	13.6	12.5
5	3	3	19.1	16.9
5	3	4	24.1	21.6
5	3	5	2.2 x	2.1
5	3	6	8.4	5.9
5	3	7	8.7	8.6
5	3	8	9.8	9.5
5	3	9	8.1	9.4
5	4	0	4.3	5.2
5	4	1	13.1	12.8
5	4	2	19.2	19.0
5	4	3	27.9	27.9
5	4	4	10.6	11.2
5	4	5	14.1	14.4
5	5	0	3.8	3.5
5	5	1	10.4	10.0
5	5	2	16.4	15.4
5	5	3	10.7	11.8
5	5	4	13.2	11.5
6	0	0	50.2	52.4
6	0	1	24.9	23.5
6	0	2	33.5	32.9
6	0	3	32.2	32.3
6	0	4	3.0	2.8
6	0	5	17.8	17.2
6	0	6	22.9	23.4
6	0	7	5.2	4.3
6	0	8	16.0	17.3
6	0	9	2.9	2.5
6	0	10	3.4	3.9
6	1	0	42.6	42.8
6	1	1	6.5	5.6
6	1	2	32.8	30.8
6	1	3	25.0	24.4
6	1	4	18.6	18.6
6	1	5	11.0	11.1
6	1	6	18.5	18.7
6	1	7	13.3	13.1
6	1	8	8.9	8.4
6	1	9	7.6	7.9
6	1	10	8.1	7.7
6	2	0	13.3	12.4
6	2	1	17.9	16.8
6	2	2	21.0	20.1
6	2	3	10.4	9.5
6	2	4	18.4	17.0
6	2	5	12.0	12.7
6	2	6	37.2	37.7
6	2	7	14.4	14.5
6	2	8	4.9	4.9
6	2	9	3.9	5.4
6	3	0	5.8	5.0
6	3	1	16.1	15.5
6	3	2	2.1 x	3.1
6	3	3	16.4	14.5
6	3	4	5.2	6.2
6	3	5	17.7	18.0
6	3	6	11.7	8.9
6	3	7	2.1 x	1.4
6	3	8	1.7 x	1.8
6	4	0	2.3 x	3.2
6	4	1	7.2	8.2
6	4	2	12.6	13.0
6	4	3	7.6	6.2
6	4	4	7.4	6.2
6	4	5	7.2	6.4
6	5	0	12.3	13.7
6	5	1	7.1	6.6
6	5	2	2.4 x	1.5
6	5	3	3.2 x	4.3
6	5	4	6.1	6.1
7	0	1	52.3	51.7
7	0	2	52.2	50.4
7	0	3	38.8	39.0
7	0	4	5.8	4.4
7	0	5	20.4	20.6
7	0	6	23.5	24.3
7	0	7	28.3	29.9
7	0	8	9.6	9.9
7	0	9	1.1 x	.8
7	0	10	.7 x	.7
7	1	0	16.7	15.4
7	1	1	61.5	61.3
7	1	2	41.1	40.5
7	1	3	48.1	47.8
7	1	4	28.9	28.0
7	1	5	16.7	17.0
7	1	6	4.2	5.1
7	1	7	11.0	10.3
7	1	8	5.8	6.3
7	1	9	5.5	5.4
7	1	10	7.9	7.0
7	2	0	16.7	16.2
7	2	1	34.9	32.5
7	2	2	33.5	31.8
7	2	3	26.6	25.5
7	2	4	11.2	10.0
7	2	5	8.6	7.4
7	2	6	2.4	3.5
7	2	7	7.9	8.2
7	2	8	11.1	9.4
7	2	9	9.0	7.4
7	3	0	20.2	20.9
7	3	1	1.8 x	1.9
7	3	2	9.3	8.8
7	3	3	7.6	7.5
7	3	4	8.0	7.7
7	3	5	14.5	14.5
7	3	6	7.1	6.2
7	3	7	8.3	8.3
7	3	8	9.5	9.2
7	4	0	14.0	14.2
7	4	1	7.1	7.0
7	4	2	12.5	12.3
7	4	3	13.1	12.9
7	4	4	10.3	10.6
7	4	5	13.4	13.6
7	5	0	9.4	10.5
7	5	1	7.6	7.4
7	5	2	4.3	5.2
7	5	3	9.7	11.1
8	0	0	15.8	13.2
8	0	1	37.0	38.6
8	0	2	27.5	24.8
8	0	3	34.0	33.8
8	0	4	23.8	23.5
8	0	5	10.3	9.4
8	0	6	5.1	5.4
8	0	7	3.3	2.4
8	0	8	16.3	16.5
8	0	9	3.3	3.2
8	0	10	14.3	14.1
8	1	0	31.3	31.6
8	1	1	16.8	15.7
8	1	2	13.2	12.8
8	1	3	18.8	17.7
8	1	4	8.9	8.0
8	1	5	20.1	20.1
8	1	6	19.0	19.6
8	1	7	15.9	15.3
8	1	8	11.0	11.0
8	1	9	13.0	11.9
8	2	0	11.5	9.3
8	2	1	6.8	6.7
8	2	2	18.5	17.8
8	2	3	17.0	16.3
8	2	4	3.8	3.1
8	2	5	5.3	5.2
8	2	6	31.2	32.2
8	2	7	17.1	16.9
8	2	8	5.9	6.1
8	2	9	3.5	3.4
8	3	0	1.9 x	2.6
8	3	1	33.3	32.9
8	3	2	20.9	21.0
8	3	3	9.6	8.6
8	3	4	10.4	12.0
8	3	5	30.7	29.5
8	3	6	11.4	9.9
8	3	7	3.6	4.0
8	3	8	6.9	5.9
8	4	0	13.2	10.1
8	4	1	7.0	8.7
8	4	2	11.8	10.0
8	4	3	12.8	12.7
8	4	4	11.2	12.2
8	4	5	5.5	3.0
8	5	0	20.4	18.7
8	5	1	1.8 x	1.8
8	5	2	4.9	5.5
8	5	3	2.8 x	3.0
9	0	1	22.0	20.8
9	0	2	29.0	27.3

Table 3 (*cont.*)

h	k	l	F_{obs}	$\lvert F_{calc}\rvert$
9	0	3	4.4	3.7
9	0	4	6.3	4.4
9	0	5	8.1	8.1
9	0	6	38.1	39.3
9	0	7	10.9	11.1
9	0	8	20.5	21.9
9	0	9	7.2	6.6
9	0	10	12.0	12.4
9	1	0	1.3x	1.1
9	1	1	30.8	29.9
9	1	2	21.9	19.8
9	1	3	8.1	7.5
9	1	4	2.7	2.1
9	1	5	18.3	17.9
9	1	6	16.1	15.2
9	1	7	14.5	14.2
9	1	8	2.8	2.4
9	1	9	4.5	4.9
9	2	0	21.8	21.7
9	2	1	1.4x	1.6
9	2	2	17.1	15.9
9	2	3	6.0	5.7
9	2	4	9.9	9.1
9	2	5	1.3x	1.3
9	2	6	13.5	13.1
9	2	7	9.5	9.6
9	2	8	5.6	5.8
9	2	9	6.8	6.1
9	3	0	15.1	15.1
9	3	1	19.3	19.4
9	3	2	16.3	15.5
9	3	3	17.6	16.0
9	3	4	12.9	12.6
9	3	5	11.8	10.4
9	3	6	13.1	12.2
9	3	7	3.5	2.8
9	3	8	9.6	10.9
9	4	0	2.2x	1.6
9	4	1	17.5	17.7
9	4	2	10.3	6.9
9	4	3	10.2	10.5
9	4	4	2.6x	2.0
9	4	5	2.0x	2.2
9	5	0	7.7	8.7
9	5	1	3.4	3.9
9	5	2	12.3	11.9
10	0	0	43.0	43.9
10	0	1	27.7	26.5
10	0	2	8.2	7.5
10	0	3	10.6	10.4
10	0	4	42.3	44.2
10	0	5	17.1	16.7
10	0	6	9.3	9.2
10	0	7	1.3x	1.2
10	0	8	12.6	13.0
10	0	9	3.4	3.1
10	1	0	32.8	32.4
10	1	1	17.3	16.7
10	1	2	39.8	38.2
10	1	3	3.6	2.9
10	1	4	19.8	20.1
10	1	5	12.2	12.0
10	1	6	24.7	25.8
10	1	7	10.3	10.9
10	1	8	10.0	10.0
10	1	9	8.9	8.5
10	2	0	30.0	28.5
10	2	1	24.9	24.5
10	2	2	13.8	14.1
10	2	3	11.4	10.4
10	2	4	16.6	16.4
10	2	5	12.1	12.7
10	2	6	17.3	18.0
10	2	7	8.9	8.3
10	2	8	8.0	8.2
10	2	9	3.1	3.5
10	3	0	3.9	3.7
10	3	1	20.7	21.7
10	3	2	31.7	32.2
10	3	3	2.3x	3.2
10	3	4	2.3x	4.2
10	3	5	9.2	10.5
10	3	6	2.1x	3.8
10	3	7	1.8x	2.6
10	3	8	4.4	5.1
10	4	0	9.9	10.3
10	4	1	11.7	10.4
10	4	2	10.0	8.0
10	4	3	9.9	8.4
10	4	4	6.5	6.5
10	4	5	5.0	6.0
10	5	0	6.5	5.5
10	5	1	10.9	9.1
10	5	2	8.0	8.4
11	0	1	3.6	3.1
11	0	2	5.7	5.5
11	0	3	7.5	6.2
11	0	4	27.9	28.5
11	0	5	9.1	9.3
11	0	6	26.5	27.3
11	0	7	12.6	12.3
11	0	8	16.8	17.8
11	0	9	2.7	2.6
11	1	0	10.1	8.5
11	1	1	17.9	17.7
11	1	2	29.6	28.3
11	1	3	8.9	7.6
11	1	4	8.6	7.4
11	1	5	14.4	14.6
11	1	6	29.9	29.1
11	1	7	11.3	10.7
11	1	8	3.6	4.3
11	1	9	3.3	3.6
11	2	0	17.7	17.6
11	2	1	5.2	4.9
11	2	2	18.1	17.6
11	2	3	14.8	13.8
11	2	4	25.0	25.7
11	2	5	8.8	8.0
11	2	6	4.1	4.0
11	2	7	1.2x	3.4
11	2	8	15.0	14.4
11	3	0	14.4	14.3
11	3	1	13.0	13.9
11	3	2	16.3	16.1
11	3	3	4.2	4.2
11	3	4	2.3x	4.3
11	3	5	25.3	24.3
11	3	6	5.2	5.7
11	3	7	9.6	10.1
11	4	0	11.7	11.5
11	4	1	2.1x	4.4
11	4	2	4.8	3.4
11	4	3	6.7	5.1
11	4	4	14.5	12.9
11	4	5	1.8x	1.4
11	5	0	7.6	9.5
11	5	1	2.2	4.0
11	5	2	8.0	7.6
12	0	0	1.4x	.9
12	0	1	42.8	42.3
12	0	2	30.8	29.1
12	0	3	1.2x	1.6
12	0	4	3.8	3.6
12	0	5	24.9	25.6
12	0	6	15.1	14.9
12	0	7	10.1	10.0
12	0	8	11.8	11.4
12	0	9	1.4	1.1
12	1	0	1.6x	1.1
12	1	1	10.9	10.2
12	1	2	23.8	22.5
12	1	3	11.9	11.2
12	1	4	15.6	14.5
12	1	5	18.0	18.3
12	1	6	10.9	10.0
12	1	7	10.6	10.2
12	1	8	4.8	5.6
12	1	9	7.3	7.1
12	2	0	4.4	4.3
12	2	1	12.7	12.7
12	2	2	7.1	7.4
12	2	3	13.7	13.3
12	2	4	10.8	10.0
12	2	5	5.9	4.8
12	2	6	6.9	7.7
12	2	7	19.0	16.8
12	2	8	2.8	3.9
12	3	0	5.1	5.6
12	3	1	22.5	23.5
12	3	2	7.8	8.1
12	3	3	7.3	8.3
12	3	4	2.3x	3.2
12	3	5	10.3	10.0
12	3	6	7.8	8.0
12	3	7	5.5	6.5
12	4	0	25.3	26.7
12	4	1	16.2	16.9
12	4	2	2.5x	2.4
12	4	3	3.4x	5.1
12	4	4	5.7	6.3
12	4	5	9.1	8.3
13	0	1	7.5	6.9
13	0	2	7.7	7.0
13	0	3	1.2x	1.5
13	0	4	29.2	30.5
13	0	5	2.3	2.4
13	0	6	11.5	12.8
13	0	7	4.8	3.9
13	0	8	2.5	2.0
13	0	9	3.0	2.7
13	1	0	14.7	13.7
13	1	1	23.9	23.1
13	1	2	11.9	10.9
13	1	3	27.3	27.7
13	1	4	16.3	14.9
13	1	5	7.8	8.2
13	1	6	8.4	7.7
13	1	7	10.5	9.0
13	1	8	3.1	4.1
13	2	0	1.7x	1.0
13	2	1	14.3	13.0
13	2	2	18.8	18.6
13	2	3	21.0	20.9
13	2	4	9.1	8.7
13	2	5	9.8	10.8
13	2	6	7.7	8.1
13	2	7	4.3	5.0
13	2	8	6.5	6.2
13	3	0	11.2	10.9
13	3	1	2.1x	4.0
13	3	2	14.1	14.5
13	3	3	7.2	6.9
13	3	4	2.2x	3.1
13	3	5	12.4	11.0
13	3	6	1.8x	1.7
13	3	7	1.3x	2.6
13	4	0	7.1	6.0
13	4	1	3.4	4.7
13	4	2	6.1	7.0
13	4	3	10.1	9.8
13	4	4	7.4	9.6
13	4	5	11.8	11.7
14	0	0	51.7	54.2
14	0	1	3.7	2.9
14	0	2	13.8	12.6
14	0	3	3.2	2.2
14	0	4	10.4	10.4
14	0	5	6.2	5.8
14	0	6	12.3	11.5
14	0	7	8.1	8.5
14	0	8	.9x	.9
14	1	0	2.8	2.7
14	1	1	26.8	25.9
14	1	2	2.9	2.9
14	1	3	19.9	20.0
14	1	4	19.3	19.1
14	1	5	9.7	9.8
14	1	6	11.9	12.5
14	1	7	3.6	3.4
14	1	8	16.5	15.8
14	2	0	7.9	6.9
14	2	1	15.4	15.9
14	2	2	8.5	9.2
14	2	3	28.1	28.4
14	2	4	11.8	11.4
14	2	5	5.2	6.1
14	2	6	10.3	10.2
14	2	7	4.3	4.4
14	2	8	3.4	2.6
14	3	0	10.2	10.1
14	3	1	11.1	11.8
14	3	2	16.2	16.6
14	3	3	2.2x	3.3
14	3	4	3.9	3.5
14	3	5	5.0	5.7
14	3	6	8.2	9.9
14	4	0	11.0	12.3
14	4	1	1.7x	4.0
14	4	2	2.2x	4.1
14	4	3	9.2	11.0
14	4	4	4.5	3.5
15	0	1	4.5	3.8
15	0	2	3.9	3.1
15	0	3	11.6	12.3
15	0	4	23.4	23.5
15	0	5	14.4	13.5
15	0	6	1.2x	.5
15	0	7	3.3	2.7
15	0	8	3.2	2.4
15	1	0	23.0	22.8
15	1	1	9.3	8.0
15	1	2	10.0	9.9
15	1	3	14.3	13.8
15	1	4	25.1	22.2
15	1	5	13.5	13.8
15	1	6	15.6	12.3
15	1	7	2.4	2.7
15	1	8	5.7	5.4
15	2	0	47.1	49.2
15	2	1	8.4	8.1
15	2	2	23.1	22.9
15	2	3	4.2	3.6
15	2	4	23.1	21.0
15	2	5	5.0	4.6
15	2	6	9.4	8.7
15	2	7	11.8	11.8
15	3	0	2.0x	3.8
15	3	1	12.5	12.7
15	3	2	4.6	5.5
15	3	3	9.6	8.9
15	3	4	6.3	6.7
15	3	5	13.7	14.6
15	3	6	1.4x	3.7
15	4	0	1.7x	2.1
15	4	1	1.6x	3.4
15	4	2	1.9x	.8
15	4	3	4.5	6.1
16	0	0	30.4	29.4
16	0	1	5.4	5.9
16	0	2	15.7	15.5
16	0	3	7.7	7.3
16	0	4	19.1	19.0
16	0	5	8.6	7.3
16	0	6	5.0	5.1
16	0	7	.9x	.6
16	0	8	.7x	.6
16	1	0	9.4	8.7
16	1	1	12.7	11.8
16	1	2	3.1	1.7
16	1	3	4.3	5.2
16	1	4	13.5	12.7
16	1	5	10.1	9.9
16	1	6	3.7	3.3
16	1	7	9.0	8.4
16	1	8	10.1	13.2
16	2	0	8.0	7.3
16	2	1	3.4	2.9
16	2	2	14.1	13.8
16	2	3	9.5	9.6
16	2	4	10.9	10.1
16	2	5	10.4	9.8
16	2	6	2.5	2.6
16	2	7	2.6	3.1
16	3	0	8.4	8.4
16	3	1	6.6	6.5
16	3	2	11.7	11.8
16	3	3	5.2	5.1
16	3	4	6.7	6.2
16	3	5	1.6x	4.4
16	4	0	1.4x	1.4
16	4	1	8.4	9.4
16	4	2	9.3	8.3
17	0	1	7.7	6.7
17	0	2	34.1	35.4
17	0	3	11.6	11.9
17	0	4	27.3	29.4
17	0	5	1.2x	.9
17	0	6	5.7	6.0
17	0	7	10.1	9.1
17	1	0	22.8	22.7
17	1	1	28.1	28.6
17	1	2	7.7	7.2
17	1	3	17.3	17.9
17	1	4	15.1	12.5
17	1	5	9.8	9.6
17	1	6	5.8	5.7
17	1	7	2.6	3.5
17	2	0	1.7x	1.0
17	2	1	6.5	6.0
17	2	2	7.8	7.5
17	2	3	6.0	5.2
17	2	4	4.8	4.7
17	2	5	11.0	9.7
17	2	6	3.9	4.5
17	3	0	9.8	10.4
17	3	1	9.8	9.2
17	3	2	4.5	3.6
17	3	3	7.6	7.5
17	3	4	9.5	9.8
17	3	5	8.1	9.3
17	4	0	7.8	6.8
17	4	1	8.0	9.7
18	0	0	21.9	20.4
18	0	1	5.7	4.8
18	0	2	10.3	10.3
18	0	3	9.3	8.2
18	0	4	8.6	8.4
18	0	5	3.9	3.9
18	0	6	.9x	1.6
18	0	7	17.3	17.2
18	1	0	4.3	5.4
18	1	1	14.5	13.3
18	1	2	9.2	7.7
18	1	3	2.9	3.5
18	1	4	9.2	9.6
18	1	5	25.8	24.9
18	1	6	2.1	2.4
18	1	7	4.0	4.9
18	2	0	1.7x	.4
18	2	1	8.5	8.0
18	2	2	6.8	6.0
18	2	3	16.0	15.2
18	2	4	7.1	7.7
18	2	5	11.7	10.2
18	2	6	4.9	4.3
18	3	0	9.2	10.8
18	3	1	6.4	7.6
18	3	2	9.5	10.6
18	3	3	1.6x	3.5
18	3	4	1.4x	3.4
19	0	1	3.2	2.7
19	0	2	15.4	15.5
19	0	3	14.8	13.7
19	0	4	3.5	3.5
19	0	5	6.5	5.7
19	0	6	6.4	6.9
19	1	0	1.9x	.9
19	1	1	9.4	7.5
19	1	2	2.9	4.5
19	1	3	3.9	5.1
19	1	4	7.7	7.7
19	1	5	3.2	3.3
19	1	6	9.5	9.5
19	2	0	30.3	28.1
19	2	1	11.6	12.0
19	2	2	5.0	5.0
19	2	3	6.5	7.8
19	2	4	5.3	5.6
19	2	5	4.1	4.6
19	3	0	2.4	2.1
19	3	1	6.4	8.1
19	3	2	4.9	5.1
19	3	3	1.3x	1.3
20	0	0	13.5	13.8
20	0	1	8.5	8.1
20	0	2	2.3x	1.2
20	0	3	14.4	14.3
20	0	4	4.1	4.3
20	0	5	3.2	2.8
20	0	6	3.0	2.4
20	1	0	10.1	10.1
20	1	1	6.7	5.3
20	1	2	3.8	3.9
20	1	3	2.5	2.7
20	1	4	5.6	5.2
20	1	5	4.3	4.2
20	2	0	10.7	10.8
20	2	1	2.0	1.9
20	2	2	6.5	5.8
20	2	3	11.9	10.8
20	2	4	7.6	7.6
20	2	5	11.8	12.3
20	3	0	9.2	10.5
20	3	1	10.3	12.7
20	3	2	1.2x	1.6
21	0	1	6.1	6.0
21	0	2	16.8	15.7
21	0	3	12.6	12.2
21	0	4	1.6	.9
21	0	5	.7x	.2
21	1	0	2.6	3.4
21	1	1	8.5	9.2
21	1	2	11.5	10.3
21	1	3	5.0	6.3
21	1	4	8.3	8.3
21	1	5	4.4	4.8
21	2	0	1.2x	.6
21	2	1	4.2	5.9
21	2	2	12.3	11.3
21	2	3	3.5	3.0
21	2	4	9.0	9.3
22	0	0	7.0	8.6
22	0	1	7.1	6.8
22	0	2	7.2	6.3
22	0	3	12.2	11.2
22	0	4	2.6	2.0
22	1	0	9.2	8.8
22	1	1	10.0	9.6
22	1	2	13.5	12.4
22	1	3	5.0	5.3
22	2	0	11.4	10.3
22	2	1	1.0x	.4
22	2	2	3.4	3.5
23	0	1	2.2	2.3
23	0	2	9.9	8.1
23	0	3	.7x	1.1
23	1	0	7.4	7.2
23	1	1	7.8	8.4
23	1	2	8.7	8.5
23	1	3	4.6	5.4
24	0	0	2.9	1.9
24	0	1	.6x	.6

Discussion

The main object of this investigation was to compare the ascorbate anion with the free acid. The relevant Tables therefore include the mean values found in ascorbic acid as well as the results from the present investigation. We have neglected the effects of anomalous scattering and of anisotropic vibrations upon the interatomic distances.

Coordination of the sodium ion

Each sodium ion is coordinated to six oxygen atoms belonging to four different ascorbate anions. The distances vary between 2·416 and 2·725 Å. The polyhedron of six oxygen atoms is a distorted octahedron. Na, O(1''''), O(3''), O(5) and O(6) form a rather corrugated equatorial plane, while O(2'''') and O(6*) are situated at the remaining corners. The arrangement is indicated in Fig. 2 by the dotted lines, and the distances and angles are given in Table 4.

Table 4. *Bond lengths* (Å) *and angles* (°) *in the polyhedron surrounding* Na

Primes and asterisks represent different equivalents of the reference atoms. Standard deviations in parentheses.

Na–O(1'''')	2·416 (4) Å
Na–O(2'''')	2·428 (4)
Na–O(3'')	2·506 (4)
Na–O(5)	2·460 (4)
Na–O(6)	2·725 (5)
Na–O(6*)	2·450 (5)
O(1'''')–Na–O(2'''')	74·3 (1)°
O(1'''')–Na–O(3'')	129·4 (1)
O(1'''')–Na–O(5)	138·3 (2)
O(1'''')–Na–O(6*)	94·9 (1)
O(1'''')–Na–O(6)	72·4 (1)
O(2'''')–Na–O(3'')	80·0 (1)
O(2'''')–Na–O(5)	109·3 (1)
O(2'''')–Na–O(6*)	147·0 (2)
O(2'''')–Na–O(6)	86·7 (1)
O(3'')—Na–O(5)	91·1 (1)
O(3'')—Na–O(6*)	83·7 (1)
O(3'')—Na–O(6)	148·6 (1)
O(5)——Na–O(6*)	99·4 (1)
O(5)——Na–O(6)	66·6 (1)
O(6*)—Na–O(6)	120·3 (2)

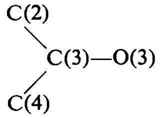
The long O(6)–Na distance of 2·725 Å may be explained by the double coordination of this alcoholic oxygen atom, as the second O(6)–Na distance is 2·450Å.

All the oxygen atoms except O(4) are engaged in this coordination and in addition they are engaged in hydrogen bonding.

The ascorbate anion

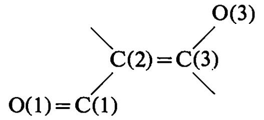
In Table 5 the distances and angles of the ascorbate anion are compared with the corresponding values in the free acid. Fig. 3 is a perspective drawing of the anion.

Examination of the ring system reveals the interesting fact that the enediol group after dissociation of the hydrogen atom at O(3) is no longer planar as in ascorbic acid. Moreover, the lactone group which was moderately corrugated in the acid is now planar within three times the standard deviation σ. In fact, the whole ring system, except for C(3) and O(3) is planar within 3σ, as seen from Table 6. If we consider the



system, this nearly defines a plane forming an angle of 8·6° to the plane part of the ring, and C(3) and O(3) lie on the same side of this plane as C(5). Measurements of the circular dichroism and nuclear magnetic resonance spectra, performed by Kresheck (1968), serve to indicate that this conformational change of ascorbic acid on ionization is maintained in aqueous solution.

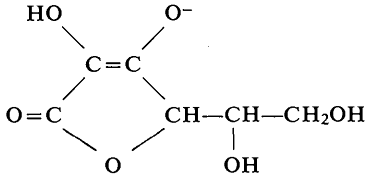
This interesting feature should be seen in view of the bonding changes that have taken place in the anion. It is evident from Table 5 that the conjugated



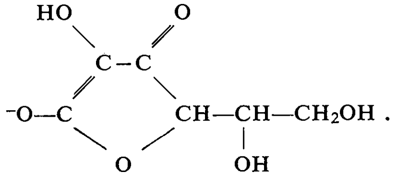
system has undergone a significant transformation on ionization, by a lengthening of the double bonds and a shortening of the single bonds. The C(2)–O(2) and C(3)–C(4) bonds have also been lengthened, presumably because of a change in the hybridization at the C(2) and C(3) atoms.

This change in hybridization is accompanied by significant changes in the angular arrangements about some ring carbon atoms. The opening of the C(4)–C(3)–O(3) angle by 5·8° is particularly striking, but the presence of the strain in the ring system complicates the analysis. In the lactone group the C(1)–O(4) and O(4)–C(4) distances and the C(1)–O(4)–C(4) angle are not affected by the ionization.

The trends mentioned above support the proposal made by Euler & Eistert (1957) that the ascorbate anion may be described as a mesomer between



and



The distances and angles in the side chain do not deviate significantly from the ideal values in the two substances, except for two dihedral angles. Firstly, the conformation about C(4)–C(5) has become almost precisely staggered, while a deviation from this ideal arrangement of 7·9° was present in ascorbic acid. The second and major change is a rotation of 101° about C(5)–C(6) relative to vitamin C, thus bringing the C(6)–O(6) direction from a near-*trans* to a near-*gauche* conformation. The sense is anticlockwise when seen from C(6) and leads to a deviation of 10·1° from an ideal staggered conformation.

Hydrogen bonding

The broken lines in Fig. 2 indicate the hydrogen bonds, showing that all the hydroxyl groups are engaged in a system that involves all the oxygen atoms

Table 5. *Distances* (Å) *and angles* (°) *in ascorbic acid and in the ascorbate anion*

Standard deviations in parentheses.

Bond	Ascorbic acid	Sodium ascorbate	Difference
C(1)–O(1)	1·216 (2) Å	1·233 (6) Å	+0·017 Å
C(2)–O(2)	1·361 (2)	1·384 (5)	+0·023
C(3)–O(3)	1·326 (3)	1·287 (5)	−0·039
C(1)–O(4)	1·355 (2)	1·358 (5)	+0·003
C(4)–O(4)	1·444 (2)	1·448 (5)	+0·004
C(5)–O(5)	1·427 (3)	1·410 (5)	−0·017
C(6)–O(6)	1·431 (4)	1·423 (5)	−0·008
C(2)–C(3)	1·338 (2)	1·373 (6)	+0·035
C(1)–C(2)	1·452 (3)	1·416 (6)	−0·036
C(3)–C(4)	1·493 (3)	1·516 (6)	+0·023
C(4)–C(5)	1·521 (4)	1·536 (6)	+0·015
C(5)–C(6)	1·521 (3)	1·503 (6)	−0·018
Angle			
C(4)–O(4)–C(1)	109·1 (2)°	108·0 (3)°	−1·1°
O(4)–C(1)–C(2)	109·5 (2)	110·6 (4)	+1·1
C(1)–C(2)–C(3)	107·8 (2)	109·5 (4)	+1·7
C(2)–C(3)–C(4)	109·5 (2)	105·8 (4)	−3·7
C(3)–C(4)–O(4)	104·0 (2)	105·2 (4)	+1·2
O(4)–C(1)–O(1)	121·4 (3)	120·4 (4)	−1·0
O(1)–C(1)–C(2)	129·1 (2)	129·0 (4)	−0·1
C(1)–C(2)–O(2)	124·6 (2)	121·6 (4)	−3·0
O(2)–C(2)–C(3)	127·5 (2)	128·7 (4)	+1·2
C(2)–C(3)–O(3)	133·5 (2)	131·3 (4)	−2·2
O(3)–C(3)–C(4)	117·1 (2)	122·9 (4)	+5·8
C(3)–C(4)–C(5)	114·8 (2)	116·1 (4)	+1·3
O(4)–C(4)–C(5)	110·4 (2)	110·3 (4)	−0·1
C(4)–C(5)–O(5)	111·7 (2)	113·4 (4)	+1·7
C(4)–C(5)–C(6)	112·7 (2)	110·1 (4)	−2·6
O(5)–C(5)–C(6)	106·9 (2)	108·5 (4)	+1·4
C(5)–C(6)–O(6)	108·0 (2)	108·5 (3)	+0·5

Table 6. *Distances* (Å) *from the best planes through parts of the ring system in the ascorbate anion and in ascorbic acid.*

Standard deviations in parentheses.

	Sodium ascorbate	Ascorbic acid		
		Molecule *A*	Molecule *B*	
O(1)	−0·0038 (40)	−0·0127 (39)	0·0192 (40)	The lactone group
O(4)	0·0021 (42)	0·0113 (35)	−0·0346 (38)	
C(1)	0·0070 (50)	0·0110 (46)	0·0008 (45)	
C(2)	−0·0056 (46)	0·0025 (45)	−0·0139 (46)	
C(4)	−0·0022 (51)	−0·0122 (49)	0·0285 (47)	
O(2)	0·0023 (36)			
C(3)	−0·1524 (44)			
O(3)	−0·3184 (38)			
O(2)	0·0131 (36)	0·0008 (37)	−0·0034 (40)	The enediol group
O(3)	0·0048 (38)	−0·0002 (41)	0·0002 (40)	
C(2)	−0·0193 (46)	−0·0014 (45)	0·0047 (46)	
C(3)	−0·0217 (44)	0·0004 (46)	−0·0008 (48)	
C(4)	0·0172 (51)	0·0004 (49)	−0·0024 (47)	
C(2)	−0·0056 (46)			
C(3)	0·0168 (44)			
C(4)	−0·0045 (51)			
O(3)	−0·0051 (38)			

except O(4). The same atoms are also coordinated to Na.

The hydrogen bond system consists of an isolated O(6)–H...O(1‴) bond, plus a sequence involving the following atoms: O(5′)–H...O(2)–H...O(3′). While O(2) participates both as donor and as acceptor of hydrogen bonds, the other oxygen atoms are either donors or acceptors only. Each ascorbate anion is thus linked to three other anions by two hydrogen bonds to each of them. If we take the sodium ion into account, a complicated network of three-dimensional interactions is revealed.

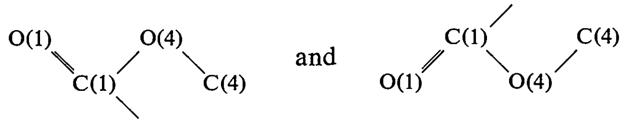
In Table 7 the distances and angles involving the hydrogen atoms are given, and even if the actual values are determined with low accuracy, they fall in the region to be expected for X-ray diffraction analyses. There is no significant deviation in any C–H bond from the mean value of 1·04 Å, nor from the average O–C–H and C–C–H angle of 109°.

A correction for polarization in the bond direction of the electron density for hydrogen is apparently desirable. The order of magnitude would presumably be the same as for ascorbic acid, where the results agreed reasonably well with the theoretical results of Stewart, Davidson & Simpson (1965).

Thermal analysis

The b_{ij} parameters in Table 2 have been used to study the vibrational ellipsoids, and it may be stated that all the atoms are clearly anisotropic. The amplitudes of of the oxygen atoms are generally somewhat larger than those of the carbon atoms, and as a rule have their major amplitudes normal to the C–O bond directions.

The C(4), O(4) and O(1) atoms have very marked anisotropic vibrations normal to the plane of the ring, while the interstitial C(1) atom has the smallest degree of anisotropy of all the atoms in the unit cell. We recall in this connexion that in the two independent molecules of ascorbic acid these atoms form alternative zigzag chains normal to the planes of the rings. The chains can be described by although the deviation from planarity is moderate.



These observations may be taken as evidence of a certain conformational lability in the lactone group, since the weak forces of hydrogen bonding may cause such changes. The atomic distances are, as we have seen, apparently very well defined.

Torsional oscillations about the C(4)–C(5) and C(5)–C(6) bonds apparently determine the vibrations of the two oxygen atoms in the side chain, since these have their largest amplitudes normal to these bonds.

The use of the form factor for hydrogen as given by Stewart, Davidson & Simpson (1965) has certainly improved the value of B for these atoms; nevertheless we find suspiciously low values for the (C)–H atoms. Although little emphasis should be laid on hydrogen parameters as determined by X-ray methods, it appears that the B values both in the present case and in ascorbic acid are systematically higher for the (O)–H atoms

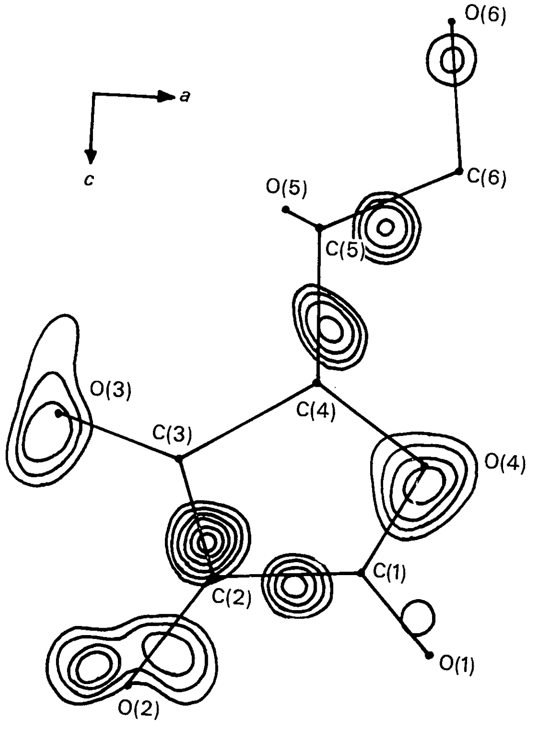


Fig. 4. Residual electron density in the region of the ascorbate anion. Contours at intervals of 0·05 e.Å^{-3}, starting at 0·2 e.Å^{-3}.

Table 7. *Distances* (Å) *and angles* (°) *involving hydrogen atoms*

	O–H	H···O	O···O	O–H···O	C–O–H
O(2)–H···O(3′)	0·83 (9)	1·75 (9)	2·546 (5)	162 (8)°	126 (6)°
O(5)–H···O(2″)	0·85 (10)	1·89 (10)	2·709 (4)	162 (10)°	110 (7)°
O(6)–H···O(1‴)	0·81 (9)	2·06 (9)	2·820 (5)	157 (10)°	112 (7)°
	C–H	C(3)–C(4)–H	C(5)–C(4)–H	O(4)–C(4)–H	
C(4)–H	1·14 (6)	111 (3)°	107 (3)°	107 (3)°	
		C(4)–C(5)–H	C(6)–C(5)–H	O(5)–C(5)–H	
C(5)–H	0·96 (5)	106 (3)°	107 (3)°	112 (3)°	
		C(5)–C(6)–H	O(6)–C(6)–H	H(1)–C(6)–H(2)	
C(6)–H(1)	1·10 (8)	113 (4)°	108 (4)°	112 (4)°	
C(6)–H(2)	0·97 (6)	105 (3)	111 (3)	–	

(average 4·7 and 5·5 Å^2) than for the (C)–H atoms (average 0·8 and 1·5 Å^2). No such trend was found in the neutron diffraction analysis of ascorbic acid.

Residual electron density

During the refinements of this structure no attempt was made to pick out one particular oxygen atom as carrier of the negative charge of the anion. The form factor was always the one given in *International Tables for X-ray Crystallography* (1962) for the free oxygen atom.

One extra electron is thus present in the anion in addition to those included in the calculations, and to conclude the analysis, a difference Fourier synthesis was evaluated. After omission of the uncertain 400 and 004 reflexions, the residual electron density in the region of the ascorbate anion is shown in Fig. 4. These maxima are clearly the largest in the unit cell, and some of them fall in the space between the carbon and oxygen atoms. This result is quite similar to that for ascorbic acid, but whether the peaks adjacent to the O(2), O(3) and O(4) atoms outside the bond area have relevance to the extra electron is questionable because of the low significance of such peaks in the present case.

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The Crystal Structure of Ribitol

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The crystal structure of ribitol, $C_5H_{12}O_5$, has been determined by means of a sign correlation procedure. The space group is $P2_1/c$ with four molecules in a unit cell with $a=8·990$, $b=4·946$, $c=15·730$ Å, $\beta=97·07°$. The crystal is a racemate mixture of left and right-handed conformers, with non-planar carbon chains. These conformers appear to be favored over that with mirror symmetry because of the non-bonding interactions between the hydroxyl groups attached to alternate carbon atoms along the chain.

Introduction

Ribitol, $C_5H_{12}O_5$, is one of the four stereoisomeric pentitols. Like xylitol, it is a *meso* form; the other two pentitols are D- and L-arabinitol. Ribitol occurs in riboflavin (vitamin B_2) where it is combined with an isoalloxazine residue, and in certain plants. The structure of the ribitol residue has been studied in two crystal structure determinations; that of the *p*-bromophenylhydrazone of ribrose by Bjåmer, Furberg & Petersen (1964), and of riboflavin hydrobromide monohydrate by Tanaka, Ashida, Sasada & Kakudo (1967). In both these structures the conformation of the polyol residue was that with a non-planar zigzag carbon chain, although the planar conformation has been found consistently in the other polyol crystal structures which have been studied, *i.e. meso*-erythritol (Shimada, 1958; Bekoe & Powell, 1959), galactitol (Berman & Rosenstein, 1968), three forms of D-mannitol (Berman, Jeffrey & Rosenstein, 1968; Kim, Jeffrey & Rosenstein, 1968) and DL-arabinitol (Hunter & Rosenstein, 1968). Galactitol is also a *meso* form, in which the potential symmetry of the molecule is not used in the crystal symmetry. In that structure the observed conformation is very close to that of the symmetrical molecule, with small distortions which could be caused by the intermolecular forces characteristic of the crystal lattice.

The primary interest in this investigation was, therefore, to determine whether the non-planar carbon chain conformation found in the isoalloxazine and *p*-bromophenylhydrazone derivatives persisted in the structure of the uncombined ribitol, and could be a structural