**177.** *The Crystalline Structure of the Sugars. Part III.*
Ascorbic Acid and Related Compounds.

By E. G. Cox and T. H. Goodwin.

PRELIMINARY X-ray and optical measurements (Cox, *Nature*, 1932, **130**, 205) were employed extensively in the elucidation of the structure of the " hexuronic acid " which Szent-Gyorgyi (*Biochem. J.*, 1928, **22**, 1387; *Nature*, 1932, **129**, 576) identified with the antiscorbutic factor, vitamin-*C*, now known as ascorbic acid, but it was considered advisable to defer detailed investigation until the constitution had been definitely established (Herbert, Hirst, Percival, Reynolds, and Smith, J., 1933, 1270). The present paper contains an account of the X-ray analysis of this compound (I), together with data for a number of related compounds, *viz.*, 2 : 3-dimethyl ascorbic acid, galacto-ascorbic acid monohydrate (II), imino-galacto-ascorbic acid (III), and 2 : 3-dimethyl gluco-ascorbic acid (IV).
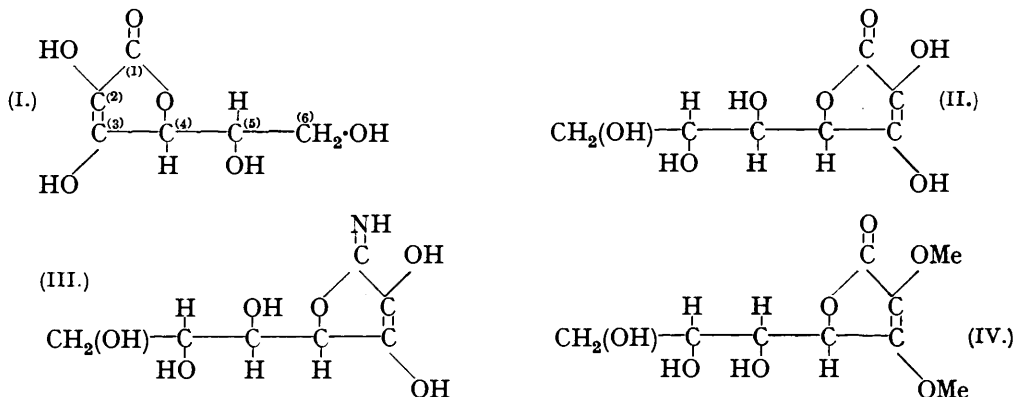

Ascorbic acid crystallises in the monoclinic system with four molecules of $C_6H_8O_6$ in the unit cell, the space group being $P2_1$, which is characterised by a two-fold screw axis parallel to the *b*-axis of the crystal. For this space group two asymmetric units per elementary cell are required, so that in this compound two molecules must be associated together in one asymmetric unit. There is no means of determining the relationship between these two molecules, except by intensity measurements, but the existence of an almost perfect halving of the {*hk*0} planes when *h* is odd strongly suggests that they are connected by a pseudo-glide plane of symmetry perpendicular to the *c*-axis. (The above-mentioned halvings might, indeed, be due to some distribution of scattering matter not involving any pseudo-symmetry, but the assumption of this additional element of symmetry is the more reasonable and is justified by the results). Since the substance is optically active, there cannot be *d*- and *l*-molecules present, and hence the molecules themselves

presumably possess a plane of symmetry, and lie in the cell so that this plane of symmetry either contains the c-axis or is perpendicular to it. (The existence of the pseudo-plane of symmetry is not inconsistent with the presence of an asymmetric carbon atom, since the efficiencies of carbon and oxygen for the scattering of X-rays are nearly the same and the hydrogen atoms may be neglected; thus, in the molecule a carbon atom may have for its " mirror image " either an oxygen atom or a hydroxyl group.)

Now, the crystals have a negative birefringence which is much higher than in any other sugar derivative so far studied. This suggests a molecule in which most of the atoms lie in one plane, this plane being perpendicular to the b-axis, since the latter is the direction of the minimum refractive index. In support of this, it is found that the intensities of the {020} reflections fall off regularly, the structure factors being roughly constant for the first three orders, as would be expected for a molecule in which most of the atoms lie in the {020} planes (see Table II).

If the molecule were quite flat, the first case mentioned above, *i.e.*, the c-axis in the plane symmetry of the molecule, would be possible, but construction of a model of formula (I) shows that the molecule, although relatively flat, is not sufficiently so to give rise to the observed pseudo halvings. (The strongest $\{\overline{2n+1}, k, 0\}$ plane observed has a structure factor less than one-tenth of the lowest recorded in Table I.) Consequently, the plane of symmetry must be perpendicular to the plane of the ring. These considerations, as pointed out by Cox and Hirst (*Nature*, 1933, **131**, 402), rule out the furancarboxylic acid structure at one time advocated by Micheel and Kraft (*ibid.*, p. 274), and also adopted by Reichstein, Grüssner, and Oppenauer in describing their synthesis of d-ascorbic acid (*Helv. Chim. Acta*, 1933, **16**, 561). Although the approximate equality of carbon and oxygen for the scattering of X-rays may be assumed, this molecule (V) cannot have a plane of symmetry either in or perpendicular to the plane of the ring.
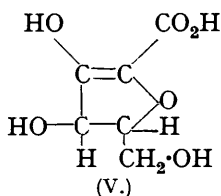
In a similar way, the enolic form of 3-ketogulopyranolactone (the pyranose molecule corresponding to ascorbic acid) cannot have a plane of symmetry either in or perpendicular to the mean plane of the ring, and is not sufficiently flat to account for the observed {020} structure factors. Ascorbic acid cannot, therefore, be a pyranose compound.

The constitution (I) established by Hirst and co-workers (*loc. cit.*), on the other hand, is not open to this objection, and if the side-chain atoms are disposed as in the figure, there is almost a plane of symmetry perpendicular to the plane of the ring, passing through C_4 and C_5 and bisecting the C_1C_2 bond. In this model C_3 and O_5 are assumed to be equivalent to O_4 and C_6 respectively, and are equidistant from the pseudo-plane of symmetry; O_3 and O_6 are also approximately equivalent.

The foregoing considerations thus lead to the conclusion that the molecules are arranged in the (020) planes with their C_1C_2 bonds parallel to the c-axis. It remains, therefore, to determine the positions of the four molecules in the unit cell and of the twelve atoms in each molecule. In theory, this can be done, without any assumptions as to the interatomic distances, by means of a sufficiently large number of measurements of reflection intensities, but in this case, the evaluation of 39 parameters is necessary even if the pseudo-glide plane is treated as a genuine one. (Corresponding atoms in the two molecules connected by the glide plane must have the same parameters parallel to the b-axis.) The crystallographic importance of ascorbic acid, however, is not sufficient to justify the labour involved, and it is more convenient to determine the molecular positions using a model such as that shown in the figure. The parameters are thus reduced to three, *viz.*, two, u_1 and w_1, fixing the position of the screw axis with respect to a reference atom in the standard molecule, and one, w_2, giving the distance of the glide plane from the same atom.

Having regard to the uncertainty as to the divergence of the valency angles in the ring from $109\frac{1}{2}°$, the simplest assumption has been made in constructing the model, *viz.*, that the ring is a regular pentagon, the angles of which are 108°, and the sides C–C and C–O are equal to 1·50 A. Outside the ring the tetrahedral angle has been maintained, and the distances C—C = 1·54 A., C—O = 1·46 A., and C=O = 1·15 A. have been adopted.

As pointed out in the earlier papers of this series (J., 1935, 978, 1495), the properties of the sugars and similar compounds suggest the occurrence of extensive association between hydroxyl groups; we have therefore assumed that the minimum distance between the oxygen atoms of hydroxyl groups is 2·5 A. in accordance with recent measurements (*e.g.*, Zachariasen, *J. Chem. Physics*, 1935, **3**, 158; Bernal and Megaw, *Proc. Roy. Soc.*, *A*, 1935, **151**, 384).   To determine whether a given arrangement of molecules is satisfactory from the point of view of space filling, it has been found advantageous to use actual models (scale 2 cm. = 1 A.) in which the hydroxyl groups are represented by spheres of radius 2·5 cm., these spheres being cut away on one side so that the correct C—O distance of 2·9 cm. can be maintained.   The carbon and oxygen atoms are represented by spheres of radius 1·5 cm.   The use of these large spheres to represent hydroxyl groups enables the models to be packed together with these spheres in contact, thus ensuring that the correct minimum O—O distance is attained.   (In a similar way spheres of radius 3·7 cm. may be used to represent methyl groups when necessary.)   Molecular arrangements involving too close approach of atoms in neighbouring molecules are readily detected in this way, and can be
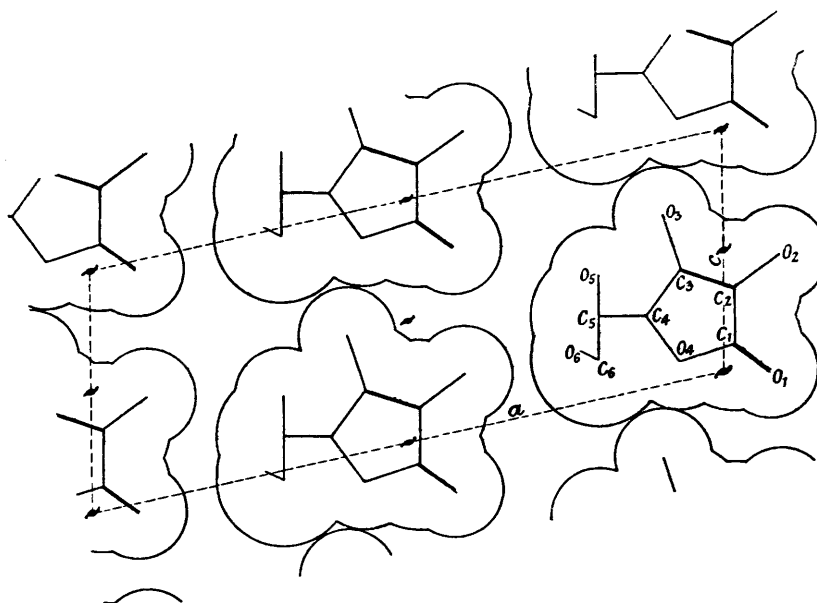
eliminated from consideration.   These models are also useful for the rapid approximate calculation of structure factors; for this purpose they are arranged in the appropriate positions and a shadow projected, by means of a beam of parallel light, on to a sheet of photographic paper, from which, after development, the atomic co-ordinates can be measured.

The structure factor F_{hkl} for any plane (*hkl*) having glancing angle θ is given by

$$F_{hkl} = \Sigma f_{\theta} e^{2\pi i(hx/a + ky/b + lz/c)} \qquad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where f_{θ} (see p. 773) is the atomic scattering factor of the atom situated at (x, y, z), summation being made over one complete unit cell.   The values of F for any structure may then be compared with those derived from the experimental intensities (I_{hkl}) by means of the formula

$$F_{hkl} = \text{const.} \times I_{hkl}^{\frac{1}{2}} . L_{\theta}^{-\frac{1}{2}} \qquad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $L_{\theta} = (1 + \cos^2 2\theta)/\sin 2\theta$.

For {*h0l*} planes, (1) reduces to $F_{h0l} = \Sigma f_{\theta} . \cos 2\pi(hx/a + lz/c)$ when the origin is taken at the intersection of the screw axis with the (010) plane.

Structure factors were calculated for the various planes by means of (1), all possible values

of the three parameters u_1, w_1, and w_2 being taken and compared with the experimental values deduced from (2). Only one combination of parameters gave reasonable agreement, and this was also found to be satisfactory from the point of view of space-filling. The molecular arrangement so obtained is shown in the figure, and the comparison of the structure factors $F_{theo.}$ and $F_{exp.}$ deduced from this structure and from the experimental data respectively is recorded in Table I for the $(h00)$ planes and in Table II for the $(0k0)$ and $(00l)$ planes. In these tables, (200) and (020) are taken as standards, and the arbitrary scale of intensity has been adjusted in each table so that $F_{theo.} = F_{exp.}$ for (200) and (020) respectively. The agreement between calculated and observed factors is satisfactory in view of the approximations made, and indicates that the molecular model adopted is substantially correct. (Various modifications of the model which have been made do not lead to any improvement in the agreement between theoretical and experimental structure factors.)

TABLE I.

$hkl.$	$f\theta_C.$	$f\theta_O.$	$I_{hkl}.$	$L\theta.$	$F_{theo.}.$	$F_{exp.}.$	$hkl.$	$f\theta_C.$	$f\theta_O.$	$I_{hkl}.$	$L\theta.$	$F_{theo.}.$	$F_{exp.}.$
200	5·37	7·74	100	10·8	33·8	34	800	2·57	4·74	5	2·2	40·3	16
400	4·22	6·80	1	5·2	3·2	5	1000	2·16	3·90	25	1·6	60·0	44
600	3·18	5·75	10	3·2	56·0	20							

TABLE II.

$hkl.$	$f\theta_C.$	$f\theta_O.$	$I_{hkl}.$	$L\theta.$	$F_{theo.}.$	$F_{exp.}.$	$hkl.$	$f\theta_C.$	$f\theta_O.$	$I_{hkl}.$	$L\theta.$	$F_{theo.}.$	$F_{exp.}.$
020	3·55	6·16	100	3·8	118 *	118	003	2·56	4·75	0·1	2·2	4·7	5
040	2·08	3·68	20	1·4	119	80	004	2·05	3·60	1	1·4	12·0	19
060	1·72	2·40	10	1·0	79·5	86	220	3·16	5·95	50	3·6	89·7	86
001	4·98	7·44	10	8·0	23·9	28	230	2·55	4·65	2	2·2	15·1	22
002	3·49	6·09	0·14	3·8	4·7	5	10$\bar{1}$	5·02	7·48	8	8·4	28·0	· 21

* For a completely flat molecule F_{020} (theo.) would be 233.

Table III gives the atomic co-ordinates for a single molecule referred to the principal axes of the cell, the origin being situated at the intersection of one of the screw axes and the plane of the molecules. If the co-ordinates of a reference atom in one molecule are $(u, v, w,)$ then the corresponding atom in the molecule which is derived from the first by the operation of the glide plane has co-ordinates $(u + 0\cdot500, v, \overline{w + 0\cdot814})$, and that in the molecule derived from the first by the action of the screw axis $(- u, \overline{v + 0\cdot500}, - w)$.

TABLE III.

Atom.	$u.$	$v.$	$w.$	Atom.	$u.$	$v.$	$w.$	Atom.	$u.$	$v.$	$w.$
C_1	0·982	0	0·106	C_3	0·068	0	0·471	C_5	0·197	0·140	0·349
O_1	0·925	0	0·976	O_3	0·095	0	0·707	O_5	0·197	0·268	0·517
C_2	0·982	0	0·349	C_4	0·121	0	0·309	C_6	0·197	0·280	0·171
O_2	0·908	0	0·455	O_4	0·068	0	0·090	O_6	0·225	0·495	0·219

The figure is a projection on (010) of two of the four molecules in the unit cell, the other two, derived from these by the screw axis, being $\frac{1}{2}b$ above. It will be seen that the molecules connected by the pseudo-glide plane are oriented so that their side chains are all in the same direction (*above* the plane of the C_4O rings) and not alternately in opposite directions; the latter arrangement would be consistent with the symmetry requirements but not with the intensities of (220) and (230). Since $\frac{1}{2}b$ is only 3·16 A. and the molecules are not completely planar, the side-chain atoms in any layer penetrate somewhat into the next layer; this accounts for the apparent gaps between the molecules in the figure. It is noteworthy that the distance between the completely flat parts of the molecules in successive layers, *i.e.*, 3·16 A., is identical with that found in maleic acid (Yardley, J., 1925, **127**, 2207). It thus appears that the carbon–carbon distance in unsaturated aliphatic compounds may be appreciably less than in aromatic substances, for the latter distance is never less than 3·4 A.

In addition, a hydrogen or hydroxyl bond appears to exist between the ring oxygen atom of one molecule and the O_3 atom of the next, the separation of these atoms being about 2·5 A. Since the former behaves neither as a true ether nor as a true lactone oxygen, this cannot be taken as evidence that similar bonds exist with ethers or lactones in general.

It should be noted finally that both *d*- and *l*-synthetic ascorbic acids have been examined

and found to be completely identical in optical properties (except rotatory power) and crystalline structure with the natural *l*-compound obtained from plant and animal sources.

Of the other compounds examined, galacto-ascorbic acid monohydrate has been studied most fully.   The presence of an additional asymmetric carbon atom in the molecule, and of water of crystallisation, together with the technical difficulties peculiar to the triclinic system, have precluded a very detailed investigation, but the optical properties and cell dimensions show that the molecule is somewhat similar to that of ascorbic acid and have enabled its orientation in the unit cell to be determined (see p. 774).

<div align="center">EXPERIMENTAL.</div>

f-Values.—For the calculation of theoretical structure factors (*F*), James and Brindley's table of atomic scattering factors (*f*) ("Internationale Tabellen zur Bestimmung von Kristall-strukturen, 1935, p. 571; *Z. Krist.*, 1931, **78**, 470) is in general use.   Their data, however, are tabulated for intervals of 0·1 in (sin θ)/λ, so that for the copper-*K*α radiation employed in this series of researches the maximum value of (sin θ)/λ is 0·65 and only seven points can be used to determine the form of the *f*-curve.   Moreover, with organic crystals small values (<0·2) of (sin θ)/λ are common, and in this region interpolation is less certain than for higher values. We have therefore calculated the *f*-values for neutral carbon and neutral oxygen for increments of 0·01 in (sin θ)/λ by the method of James and Brindley from data given by them (*Phil. Mag.*, 1931, **12**, 81, Tables I, II, and III).   For carbon, the following values of the screening constants (*s*) were used : (1,0) electrons, *s* = 0·36; (2,0) electrons, *s* = 2·6; (2,1) electrons, *s* = 4·1.   The *f*-values are shown in Table IV as functions of (sin θ)/λ, and in Table V as functions of *d*, the lattice spacing.   No temperature factor has been applied to the results.

<div align="center">TABLE IV.</div>

(sin θ)/λ.	f_C.	f_O.	(sin θ)/λ.	f_C.	f_O.	(sin θ)/λ.	f_C.	f_O.	(sin θ)/λ.	f_C.	f_O.
0	6·00	8·00	0·18	3·23	5·75	0·36	1·89	3·24	0·54	1·63	2·07
0·01	5·99	8·00	0·19	3·05	5·59	0·37	1·86	3·14	0·55	1·61	2·05
0·02	5·95	7·98	0·20	2·97	5·42	0·38	1·83	3·05	0·56	1·60	2·01
0·03	5·84	7·95	0·21	2·87	5·23	0·39	1·81	2·96	0·57	1·59	1·99
0·04	5·71	7·89	0·22	2·76	5·08	0·40	1·80	2·87	0·58	1·58	1·96
0·05	5·58	7·83	0·23	2·66	4·91	0·41	1·78	2·80	0·59	1·56	1·94
0·06	5·38	7·74	0·24	2·58	4·75	0·42	1·77	2·72	0·60	1·55	1·91
0·07	5·20	7·61	0·25	2·50	4·61	0·43	1·75	2·64	0·61	1·54	1·89
0·08	5·00	7·46	0·26	2·42	4·46	0·44	1·74	2·57	0·62	1·53	1·87
0·09	4·80	7·31	0·27	2·35	4·32	0·45	1·73	2·52	0·63	1·51	1·84
0·10	4·60	7·20	0·28	2·28	4·18	0·46	1·72	2·48	0·64	1·50	1·83
0·11	4·40	7·00	0·29	2·21	4·04	0·47	1·71	2·42	0·65	1·49	1·81
0·12	4·21	6·80	0·30	2·16	3·90	0·48	1·70	2·36	0·66	1·47	1·80
0·13	4·04	6·64	0·31	2·11	3·77	0·49	1·68	2·30	0·67	1·45	1·78
0·14	3·85	6·47	0·32	2·05	3·65	0·50	1·67	2·25	0·68	1·44	1·76
0·15	3·69	6·29	0·33	2·01	3·54	0·51	1·66	2·21	0·69	1·42	1·75
0·16	3·53	6·11	0·34	1·96	3·43	0·52	1·65	2·17	0·70	1·40	1·74
0·17	3·37	5·93	0·35	1·93	3·34	0·53	1·64	2·12			

<div align="center">TABLE V.</div>

d.	f_C.	f_O.	*d*.	f_C.	f_O.	*d*.	f_C.	f_O.	*d*.	f_C.	f_O.
0·7	1·37	1·73	1·9	2·39	4·43	3·0	3·41	6·00	5·5	4·79	7·31
0·8	1·53	1·86	2·0	2·50	4·61	3·2	3·59	6·19	6·0	4·94	7·42
0·9	1·61	2·04	2·1	2·60	4·81	3·4	3·73	6·35	7·0	5·16	7·60
1·0	1·67	2·23	2·2	2·69	4·99	3·6	3·87	6·49	8·0	5·33	7·72
1·1	1·74	2·50	2·3	2·78	5·13	3·8	4·00	6·61	9·0	5·46	7·78
1·2	1·79	2·75	2·4	2·87	5·29	4·0	4·13	6·73	10·0	5·57	7·83
1·3	1·83	3·00	2·5	2·96	5·43	4·2	4·25	6·84	12·0	5·68	7·89
1·4	1·90	3·25	2·6	3·05	5·56	4·4	4·35	6·94	14·0	5·76	7·91
1·5	1·99	3·50	2·7	3·14	5·67	4·6	4·44	7·03	16·0	5·82	7·93
1·6	2·09	3·75	2·8	3·23	5·79	4·8	4·51	7·11	20·0	5·89	7·95
1·7	2·19	4·00	2·9	3·31	5·90	5·0	4·60	7·20	50·0	5·99	8·00
1·8	2·29	4·23									

These values are not strictly reliable for a substance such as ascorbic acid containing several doubly bound atoms, but are probably sufficiently accurate in view of the other approximations which must necessarily be made at this stage in the analysis of the compound.

l-Ascorbic Acid (I).—For the earlier work, portions of the same samples used to establish

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the constitution (Hirst and co-workers, *loc. cit.*) were employed; these had been prepared from adrenal glands and from paprica.   Later X-ray and optical measurements confirmed that the synthetic *l*-ascorbic acid is identical with the natural product, and that the synthetic *d*-acid is also indistinguishable from it except in rotatory power.   Crystallisation from several solvents and under a variety of conditions gave no indication of dimorphism; characteristic square or slightly elongated crystals, similar to those originally described by Szent-Gyorgyi (*Biochem. J.*, 1928, **22**, 1408, Fig. 2a) were invariably obtained.   These are monoclinic, tabular on *a* {100}, and exhibit the forms *r* {101}, *s* {$\bar{2}$01}, and *p* {210}.   The approximate equality of the angles *a* : *r* (59°) and *a* : *s* (61°) gives the crystals a pseudo-orthorhombic habit, which supports the view that the additional X-ray halvings which are observed are due to a pseudo-plane of symmetry perpendicular to the *c*-axis.

The cell dimensions are $a = 16{\cdot}95$, $b = 6{\cdot}32$, $c = 6{\cdot}38$ A., and $\beta = 102\frac{1}{2}°$.   The number (n) of molecules in the unit cell is four; d (calc.) $= 1{\cdot}74$ g./c.c. (obs. $= 1{\cdot}74$).   Oscillation photographs show that {010} is halved, and that all {*hk*0} planes for which *h* is odd are either absent or exceedingly weak.   The space group is therefore $P2_1$ (C_2^2); the significance of the {*hk*0} halvings has been discussed on p. 769.   The intensities of the various reflections recorded in Tables I and II were measured on an arbitrary scale by photographic comparison, a strong reflection being reduced in a known ratio by means of aluminium absorbing screens until equal to a weaker one as judged by eye.   Since the best available crystals were quite small, these measurements are probably not accurate to more than 10—20%.

The refractive indices, determined by immersion methods, are $\alpha = 1{\cdot}476 \pm 0{\cdot}002$, $\beta = 1{\cdot}594 \pm 0{\cdot}002$, and $\gamma = 1{\cdot}750 \pm 0{\cdot}005$.   (All refractive indices recorded in this paper are for the sodium-*D* wave-length.) γ is the acute bisectrix (*i.e.*, the crystals are optically positive) and α is parallel to [*b*].   The plane of the optic axes is perpendicular to (010) and inclined at $42° \pm 2°$ to (100).   Owing to the difficulty of distinguishing between *r* and *s*, it was not determined whether the above angle is in the acute or the obtuse angle β.   The above refractive indices may be compared with the values $\alpha = 1{\cdot}465$, $\beta = 1{\cdot}600$, and $\gamma = 1{\cdot}747$ for $\lambda = 5461$ A. given by Hendricks (*Nature*, 1934, **133**, 178).

It is of interest to note that the mean molecular refractivity of crystalline ascorbic acid, calculated for sodium light by the Lorentz–Lorenz equation, is 34·7, which is in good agreement with the theoretical value 35·0.   On the other hand, the theoretical value for the ketonic forms of ascorbic acid would be 33·9.

d-Galacto-ascorbic Acid Monohydrate (II).—This compound (Baird, Haworth, Herbert, Hirst, Smith, and Stacey, J., 1934, 65) crystallises from water in large but rather poor triclinic asymmetric crystals.   The best crystal measured exhibited the forms *a* {100}, *a'* {$\bar{1}$00}, *b* {010}, *b'* {0$\bar{1}$0}, *c* {001}, *c'* {00$\bar{1}$}, *m* {110}, and *p'* {0$\bar{1}$1}.   Goniometric measurements were made to identify the above faces, but were not sufficiently accurate for the calculation of reliable axial ratios.   Actually, a number of interfacial angles was measured with an accuracy of $\frac{1}{4}°$ by means of series of Laue photographs, each series consisting of several exposures in which the angular setting of the crystal differed by successive $\frac{1}{2}°$ intervals.   In some cases more accurate values were obtained by means of the ionisation spectrometer.   The lengths of the various axes were determined from rotation photographs, and the primitive cell deduced from them was confirmed by the spectrometer measurements and by oscillations about the *b*- and *c*-axes.

The cell dimensions are $a = 5{\cdot}96$, $b = 8{\cdot}56$, $c = 4{\cdot}75$ A. (whence $a : b : c = 0{\cdot}6966 : 1 : 0{\cdot}5551$), $\alpha = 91° 48'$, $\beta = 102° 23'$, and $\gamma = 79° 06'$; $n = 1$; d (calc.) $= 1{\cdot}60$ g./c.c. (obs. $= 1{\cdot}60$).   Space group $P1$ (C_1^1).   The principal interfacial angles measured on the ionisation spectrometer are *a* (100) : *b* (010) $= 100° 45\frac{1}{2}'$, *b* (010) : *c* (001) $= 90° 33'$, *c* (001) : *a* (100) $= 77° 44\frac{1}{2}'$, and *a* (100) : *q* (1$\bar{1}$0) $= 30° 40\frac{1}{2}'$ (calc. $= 30° 39\frac{1}{2}'$).

The refractive indices are $\alpha = 1{\cdot}46$, $\beta = 1{\cdot}57$, and $\gamma = 1{\cdot}68$.   The minimum refractive index, α, is inclined at $30° \pm 5°$ to the normal to *c* (001) and at $74° \pm 5°$ to the normal to *b'* (0$\bar{1}$0).   Assuming that the mean plane of the molecule is perpendicular to α, the molecular " thickness " is about 3·6 A.

d-Imino-galacto-ascorbic Acid (III).—Large crystals of this compound (Haworth, Hirst, Jones, and Smith, J., 1934, 1197) were available, but all were found to be twinned.   They are apparently orthorhombic pseudo-tetragonal combinations of *p* {104}, *q* {014}, and *c* {001}, fully developed and twinned on *m* {110}, which occasionally appears as a partially developed form.   The lines of junction of the individual crystals in a twin are visible on *c* {001}, but they are not parallel to any simple crystallographic axes.

Through *c* {001} can be seen in convergent polarised light a centred acute bisectrix figure which turns through 90° when one of the above-mentioned junction lines is crossed.   The sign

is positive, the refractive indices being $\alpha = \beta = 1\cdot623 \pm 0\cdot002$, $\gamma = 1\cdot64$ ($\beta - \alpha = 0\cdot001$). The optic axial angle is $2E = 47°$, and there is strong dispersion of the optic axes ($\rho > \upsilon$).

Goniometric measurements gave the following results :

	Obs.	Calc.
c (001) : p (104) =	55° 16′	—
c (001) : q (014) =	55 10	—
p (104) : q (014) =	70 36	71° 00′
q (014) : m (110) = *ca.* 55		54 30

The difference between $c : p$ and $c : q$ is probably not significant; if both are assumed to be equal to $55° 13′$ the axial ratios are $a : b : c = 1\cdot000 : 1 : 5\cdot758$.

X-Ray rotation photographs about the a and b axes are indistinguishable; the cell dimensions are $a = b = 6\cdot7$, $c = 38\cdot5$ A., whence $a : b : c = 1\cdot00 : 1 : 5\cdot74$ (cf. goniometric values above); $n = 8$; d (calc.) $= 1\cdot58$ g./c.c. (obs. $1\cdot58$). In view of the large number of molecules in the unit cell and the difficulties caused by twinning, the importance of the substance did not appear sufficient to warrant further investigation.

Dimethyl d-*Gluco-ascorbic Acid* (IV).—Fairly good, but very small crystals of this compound {m. p. 94°, $[\alpha]_D = - 22°$ in water ($c, 4\cdot0$)} were supplied by Mr. J. K. N. Jones of this laboratory. They are elongated monoclinic combinations of a {100} and R {10$\bar{1}$}, terminated by m {011}. The cell dimensions are $a = 9\cdot66$, $b = 7\cdot70$, $c = 8\cdot77$, and [102] = $15\cdot89$ A., whence $\beta = 115° 59′$ and $a : b : c = 1\cdot254 : 1 : 1\cdot139$; $n = 2$; d (calc.) $= 1\cdot43$ g./c.c. (obs. $1\cdot45$). The space group is $P2_1$ (C_2^2). The refractive indices are $\alpha = 1\cdot46$ (parallel to the b-axis) and $\gamma = 1\cdot60$. These data suggest that the molecules are relatively flat and lie in the (020) planes (thickness $\frac{1}{2}b$, *i.e.*, $3\cdot85$ A.).

SUMMARY.

A crystallographic examination of ascorbic acid has been made, and a structure which is in good accord with the optical properties and *X*-ray reflection intensities is proposed. In connection with this and similar work it has been considered advisable to calculate atomic scattering factors for carbon and oxygen for smaller intervals of (sin θ)/λ than those normally available : tables of f for intervals of $0\cdot01$ in (sin θ)/λ are given in the experimental part of the paper. *X*-Ray data are also recorded for some substances related to ascorbic acid.