The value of the integral (2) for the area DP_1IO can be calculated and reduced to the form:

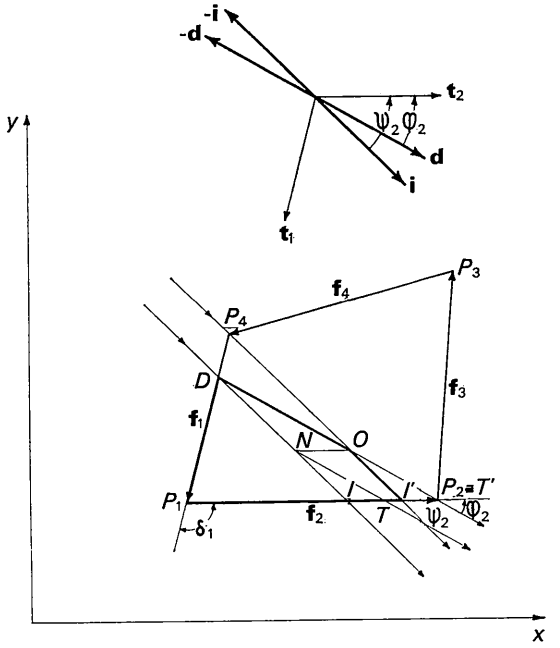


Fig. 4. Calculation of $(e.d.a.)_{DP_1IO}$. General case. $l_D=DN+NT$, $l_O=P_4O+OP_2$, $l_I=P_4I$, $l_{P_1}=0$

$$(e.d.a.)_{DP_1IO} = \frac{1}{\mu^2}\left[OD \,.\, DP_1 \sin O\hat{D}P_1 \frac{\exp(-\mu l_D)}{(l_D-l_O)(l_D-l_{P_1})} + DP_1 \,.\, P_1I \sin D\hat{P}_1I \frac{\exp(-\mu l_{P_1})}{(l_{P_1}-l_D)(l_{P_1}-l_I)} + P_1I \,.\, IO \sin P_1\hat{I}O \frac{\exp(-\mu l_I)}{(l_I-l_{P_1})(l_I-l_O)} + IO \,.\, OD \sin I\hat{O}D \frac{\exp(-\mu l_O)}{(l_O-l_I)(l_O-l_D)}\right], \quad (24)$$

where l_D, l_{P_1}, l_I, l_O are path lengths at the corner of the area. Expression (24) is independent of the reference system and depends only on the contour of the area. The total $(e.d.a.)_{2,2}$ is of the form $(A/B)\exp(-C)$, each corner contributing one term to the sum.

References

BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180.
EVANS, H. T. (1952). *J. Appl. Phys.* **23**, 663.
FERRARI, A., BRAIBANTI, A. & TIRIPICCHIO, A. (1961). *Acta Cryst.* **14**, 1089.
FERRARI, A., BRAIBANTI, A. & TIRIPICCHIO, A. (1965). *Acta Cryst.* **18**, 45.
JEFFERY, J. W. & ROSE, K. M. (1964). *Acta Cryst.* **17**, 343.
WELLS, M. (1960). *Acta Cryst.* **13**, 722.

Acta Cryst. (1965). **19**, 103

The Crystal Structure of Calcium 5-Keto-D-Gluconate (Calcium D-*xylo*-5-Hexulosonate)

BY A. A. BALCHIN* AND C. H. CARLISLE

Birkbeck College, Department of Crystallography, Malet Street, London, W.C. 1, England

(*Received* 14 *August* 1964)

Crystals of calcium 5-keto-D-gluconate, $Ca(C_6H_9O_7)_2 \,.\, 2H_2O$ are monoclinic, space-group $A2$, with $a=9{\cdot}39$, $b=8{\cdot}03$, $c=12{\cdot}37$ Å; $\beta=107{\cdot}9°$; $Z=2$.

The structure, determined by three-dimensional Fourier methods, exhibits a lactol arrangement of the 5-keto-D-gluconate ion, with eightfold coordination of the calcium atom (Ca – O, 2·46 Å; Ca – H_2O, 2·39 Å). The metal ion is chelated by two organic ions. The molecules form strongly bonded sheets, parallel to the (100) plane, held weakly together by hydrogen linkages. Ring closure occurs in the organic ion between C(2) and C(5), resulting in a (non-planar) furanoid ring with a new asymmetric centre at C(5), yielding a C(4),C(5) *cis* diol. The structure has been refined to an R index of 0·12 for the 1022 observed reflexions.

Cell dimensions are given also for calcium 2-keto-D-gluconate, (calcium D-*arabino*-hexulosonate), $Ca(C_6H_9O_7)_2 \,.\, 3H_2O$; $P2_12_12_1$; $a=10{\cdot}43$, $b=18{\cdot}33$, $c=9{\cdot}50$ Å; $Z=4$, and possible structural relationships between the two compounds are discussed.

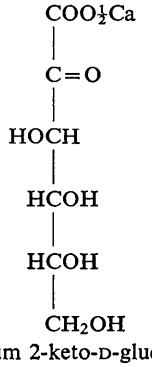
Introduction

The sugar acids have been shown to be particularly effective as sequestrants for calcium ions from alkaline solution, their affinity for calcium being attributed to the formation, through coordinate and covalent bonds, of chelated rings between the metallic ions and the hydroxyl and carboxyl groups of the acid (Prescott, Shaw, Bilello & Cragwall, 1953; Mehltretter, Alexander & Rist, 1953). The identification of calcium 2-keto-gluconate in the growth products of micro-organisms

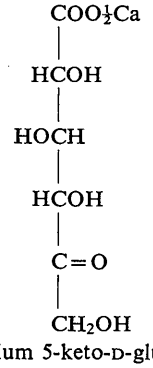
* Present address: Department of Applied Physics, Brighton College of Technology, England.

found in soil and in the rhizospheres of plants, when grown in media containing glucose and water-insoluble calcareous minerals, suggested to Duff & Webley (1959) that chelation of calcium by 2-ketogluconic acid could play an important part in the weathering and solubilization of natural silicates and other soil material, the acid being formed by bacterial action in the soil.

Both calcium 2-ketogluconate and calcium 5-ketogluconate may be formed by the action of bacteria on liquors containing glucose and calcium carbonate. According to Stubbs, Lockwood, Roe, Tobenkin & Ward (1940) the specificity of the organism is the deciding factor determining the product, but the results of Bernhauer & Knobloch (1940) indicate that both the strain of organism employed and the substrate material may influence the resulting product. Chemically the two salts differ only in the position of the ketone group:



Calcium 2-keto-D-gluconate.



Calcium 5-keto-D-gluconate.

and it has been suggested that the greater sequestration of calcium by 2-ketogluconic acid (in comparison with 5-ketogluconic acid or with gluconic acid) may be attributable to the closer proximity in this compound of the ketone and carboxyl groups.

Although the conformation of the gluconate ion has been established (Littleton, 1953) no investigation of the postulated chelating action of ketogluconate ions has yet been reported. In order to determine the nature of the bonding between the ions of calcium and of the ketogluconates, the crystal structures of the two compounds above are being studied; this paper reports the results recorded for calcium 5-ketogluconate.

Crystal data and structure cell dimensions of calcium 5-keto-D-gluconate

The composition of this compound has been quoted as $Ca(C_6H_9O_7)_2 . 2\frac{1}{2}H_2O$ (Stubbs *et al.* 1940) or as $Ca(C_6H_9O_7)_2 . 3H_2O$ (Kiliani, 1922).

The material used for the present work was recrystallized by slow precipitation from warm aqueous solution, either by cooling or by addition of ethanol. Both methods of preparation yielded elongated monoclinic crystals of the same habit, bounded by dominating faces $\{\bar{1}02\}$ and $\{100\}$, and with a uniterminal development characteristic of class 2.

The crystals are transparent, colourless, biaxial, optically negative, with β (the intermediate refractive index) parallel to the unique axis b, and γ almost parallel to c. On crushing between glass plates they shatter into thin needles, with easy cleavages parallel to b.

The dimensions of the unit cell, measured from oscillation photographs taken with Cu $K\alpha$ radiation of wavelength 1·542 Å, are $a = 9{\cdot}39 \pm 0{\cdot}04$, $b = 8{\cdot}03 \pm 0{\cdot}02$, $c = 12{\cdot}37 \pm 0{\cdot}05$ Å; $\beta = 107{\cdot}9° \pm 1{\cdot}3°$ and the density D_m of the crystals, measured by flotation, is $1{\cdot}75 \pm 0{\cdot}02$ g.cm^{-3}.

The crystals are therefore assigned a molecular composition $Ca(C_6H_9O_7)_2 . 2H_2O$ with two molecules per unit cell, giving $D_x = 1{\cdot}735$ g.cm^{-3}.

Systematic absences were observed in the X-ray reflexions for hkl, $(k+l)$ odd, suggesting that the space group is $A2$. This space group requires the calcium ions to lie in special positions along the diad axes, and also that the unit cell should contain an even number of water molecules.

Examination of crystals for optical activity, or for pyroelectricity, the presence of which might be expected in a material of this symmetry, were inconclusive, possibly because of the small size of the available specimens. Alternative space groups Am and $A2/m$ were considered, but eventually discarded as these would require the molecules to show mirror symmetry.

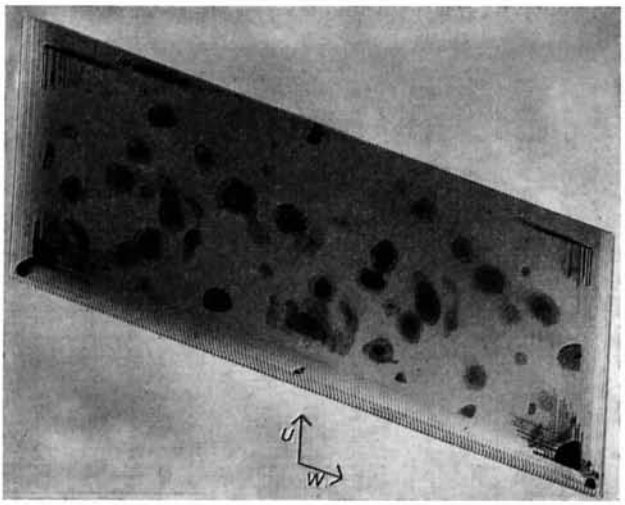
Structure determination

Relative X-ray intensities were estimated from equi-inclination Weissenberg photographs, taken with Cu $K\alpha$ radiation on multiple film packs, by visual comparison with a series of timed exposures of a single reflexion. Independent estimates of the intensities of symmetrically related reflexions did not normally deviate by more than 5% from their arithmetic mean. Intensities were assigned to 1022 non-equivalent reflexions.

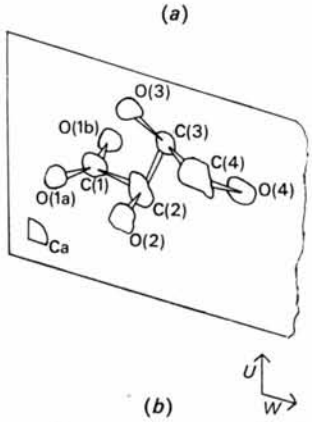
Corrections for Lorentz and polarization effects were applied from Cochran charts (Cochran, 1948). The irregular shape of the crystals made absorption corrections difficult to apply, so very small crystals (cross section not greater than 0·2 mm × 0·2 mm) were chosen to minimize errors from this cause. The corrected intensities were scaled to approximately absolute values by Wilson's (1942) method and were afterwards adjusted as the structure became known. In the initial stages of structure factor calculation a mean isotropic temperature factor, $B = 1{\cdot}69$, was used.

The calcium ions, because of their special positions, cannot unambiguously define the phases of the structure amplitudes of this non-centrosymmetrical crystal. A three-dimensional electron density map phased on the scattering contributions only of these ions would exhibit the same $2/m$ symmetry as the Patterson vector function and its interpretation would not have been free of ambiguity.

Since the stereochemistry of the 5-keto-D-gluconate ion was, at this stage, uncertain, it was thought advis-



(*a*)



(*b*)

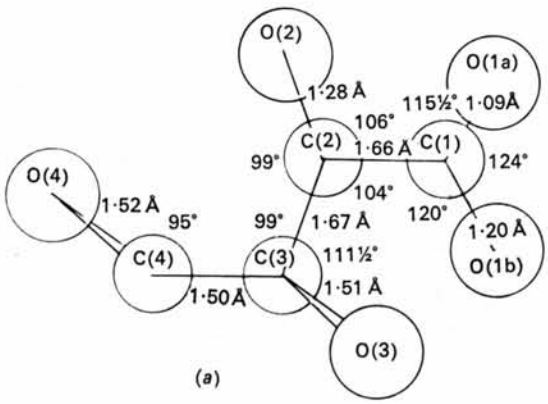
Fig. 1. Calcium 5-keto-D-gluconate. (*a*) Patterson function sectioned at intervals of 1/30th along *V*. (*b*) Plan of resolved peaks showing recognizable stereochemical features.

able to study the Patterson vector function in some detail. Sharpening of the Patterson diagram was effected by dividing each Patterson coefficient by the mean square structure amplitude, obtained from the Wilson curve, for the appropriate range of d^*. Sharpened Patterson projections on (001) and (010) were uninterpretable and the analysis was therefore concentrated on the three-dimensional sharpened function using the complete set of data. Sections were calculated at intervals of 1/30th. along the *V* axis, and Fig. 1 shows the resulting vector distribution traced on to Perspex sheets and stacked along *V*.

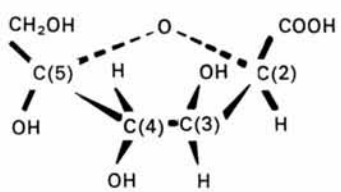
The attempt was made, accordingly, to identify recognizable features incorporating organic stereochemical principles directly from the Patterson function because the more prominent vectors here would very likely be those between the calcium atom and the other lighter atoms. On this argument an examination of these peaks should yield some information about the stereochemistry of the organic molecule.

Nine peaks are clearly resolved, in the Patterson function, in locations consistent with part of a carbon chain terminated by a carboxyl group. The spatial relationship of these peaks is shown in Fig. 2(*a*). The further location of atomic sites from these maps could not be reconciled with a straight chain model, as put forward for the gluconate ion by Littleton (1953). Examination of the partially resolved vector peaks near the plane $V=0$ suggested the structure shown in Fig. 2(*b*), the five-membered ring configuration maintaining tetrahedral coordination around the carbon atoms.

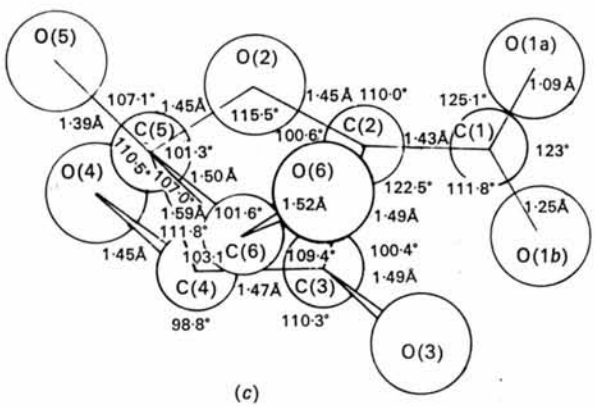
Phases for the observed structure amplitudes were therefore calculated from the positions of the nine clearly resolved atomic sites shown in Fig. 2(*a*), and these were used to construct a partial three-dimensional electron density map. This Fourier diagram, besides revealing the nine sites used in calculating phases, showed low peaks indicating the possible positions of the remaining six atoms. The final selection of all



(*a*)



(*b*)



(*c*)

Fig. 2. (*a*) Configuration of nine atomic sites located on Patterson diagram. (*b*) Stereochemical formula consistent with non-resolved vector peaks. (*c*) Configuration of 5-keto-D-gluconate ion from partially-phased electron density map.

Table 1. *Structure factors for calcium 5-ketogluconate*

Each line contains *h*, *k*, *l*, 100 F_{obs}, 100 F_{calc}.

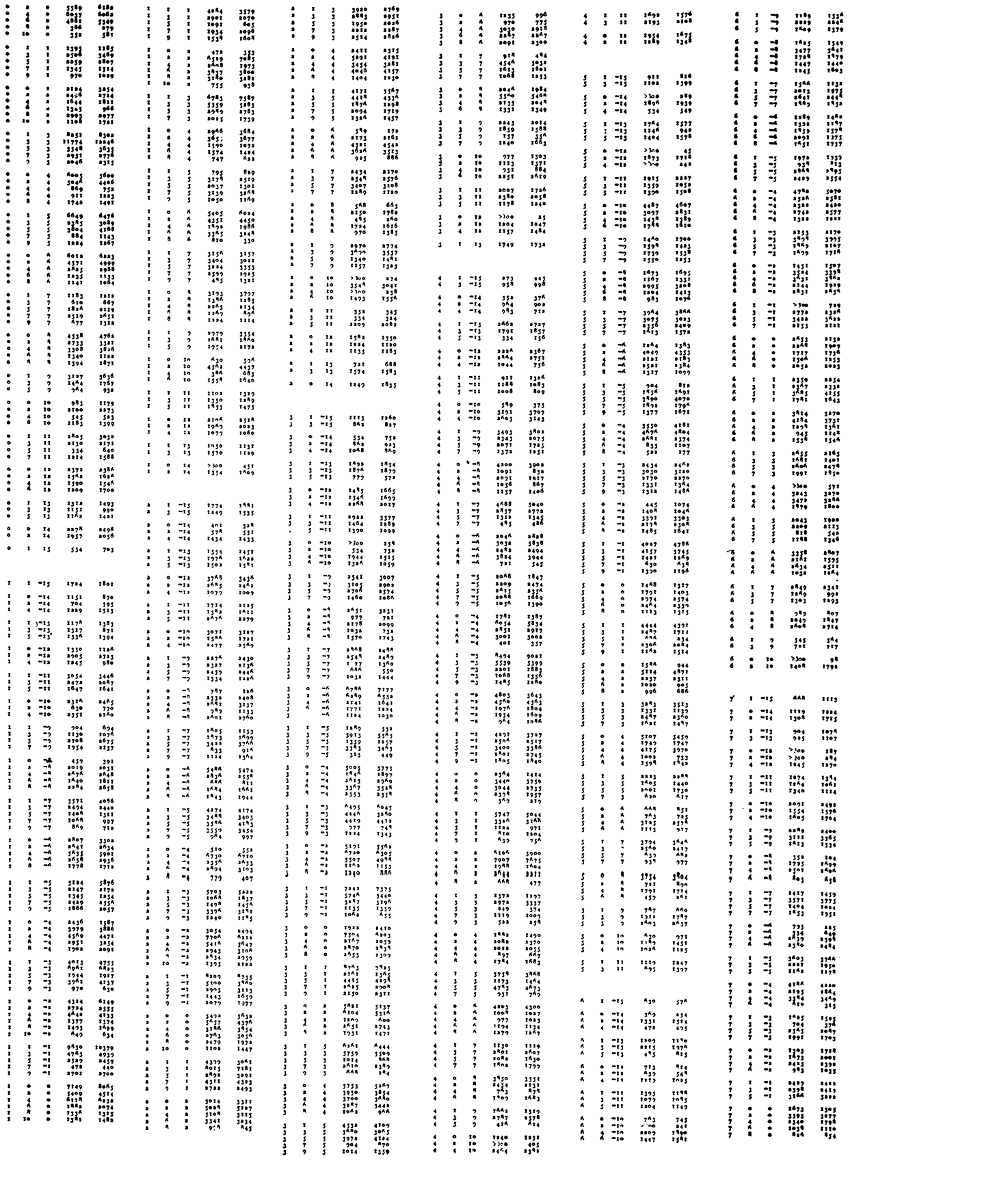
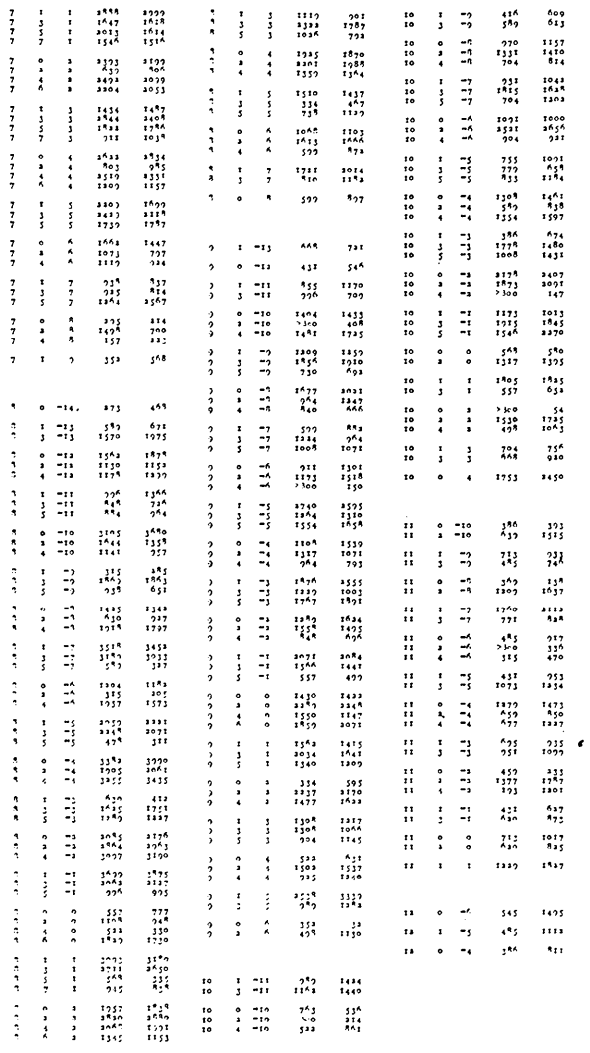


Table 1 (*cont.*)



fifteen atomic sites, as indicated in Fig. 2(*c*), gave calculated structure factors in reasonable agreement with those observed, yielding an R index of 20%.

Four cycles of least-squares refinement, reducing R to 11% (including zero reflexions), were performed on a Ferranti MERCURY computer, with programs described by Mills & Rollett (1961). For the carbon and oxygen atoms the scattering factors of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) were used, and for the calcium ion that of James & Brindley (1931). Comparison of $|F_{obs}|$ and $|F_{calc}|$ is made in Table 1.

Desription of structure

The asymmetric unit of the structure of calcium 5-keto-D-gluconate is shown in Fig. 3(*a*) and a schematic *b*-axis projection in Fig. 3(*b*). Atomic coordinates are listed, with estimated standard deviations, in Table 2. In Table 3 are listed the components of the mean square vibration amplitude tensor, U_{ij}, calculated from the anisotropic temperature factors of the atoms; since no corrections have been applied for absorption in the crystal these values are only approximate, and estimates of standard deviations have not been made. Intramolecular bond lengths and angles are given, with estimated standard deviations, in Table 4.

The 5-ketogluconate ion consists of an almost planar five-membered furanoid ring –C(2)–C(3)–C(4)–C(5)–O(2)– with a carboxylate ion attached to C(2) and with –OH and $-CH_2OH$ groups arranged tetrahedrally at C(5). The carboxylate ion, and the hydroxyl group at C(5), are near the plane of the ring. The –OH group at C(3) and the $-CH_2OH$ group at C(5) lie away from this plane, but on the same side of it, and the –OH group at C(4) lies at a similar distance on the opposite side. The new asymmetric centre at C(5) has formed to give a C(4),C(5) *cis* diol. C(2) lies slightly above the plane defined by the other four members of the ring.

Stereochemically the lactol ring is comparable to the furanoid rings described by Beevers & Cochran (1947) in the structure of sucrose sodium bromide dihydrate, and by Furberg in the structures of cytidine (Furberg, 1950) and cytidilic acid *b* (Alver & Furberg 1959). The puckering of the ring is similar to that found in cytid-

Table 2. *Atomic coordinates and estimated standard deviations in the space group A2 for calcium 5-ketogluconate*

	x/a	*y/b*	*z/c*
Ca	0·0000 ± 0·0000	0·0000 ± 0·0006	0·0000 ± 0·0000
O(1*a*)	0·1538 ± 0·0010	−0·2525 ± 0·0012	0·0271 ± 0·0007
O(1*b*)	0·3136 ± 0·0010	−0·4328 ± 0·0013	0·1360 ± 0·0007
O(2)	0·1279 ± 0·0009	−0·0760 ± 0·0011	0·1996 ± 0·0007
O(3)	0·4371 ± 0·0010	−0·0513 ± 0·0013	0·2168 ± 0·0008
O(4)	0·3101 ± 0·0011	−0·1052 ± 0·0013	0·4603 ± 0·0008
O(5)	0·0598 ± 0·0010	0·0453 ± 0·0012	0·3396 ± 0·0008
O(6)	0·0548 ± 0·0010	0·2341 ± 0·0013	0·1345 ± 0·0008
C(1)	0·2308 ± 0·0014	−0·3035 ± 0·0017	0·1204 ± 0·0011
C(2)	0·2305 ± 0·0014	−0·2160 ± 0·0017	0·2269 ± 0·0011
C(3)	0·3778 ± 0·0014	−0·1365 ± 0·0018	0·2942 ± 0·0011
C(4)	0·3260 ± 0·0013	−0·0145 ± 0·0019	0·3672 ± 0·0010
C(5)	0·1722 ± 0·0014	0·0477 ± 0·0017	0·2882 ± 0·0010
C(6)	0·1810 ± 0·0014	0·2151 ± 0·0018	0·2348 ± 0·001
H_2O	0·2407 ± 0·0011	−0·4235 ± 0·0014	0·4884 ± 0·0009
(*W*)	*0·500*	*−0·135*	*0·000*

ilic acid *b*, but the dispositions of the hydroxyl groups on C(3) and C(4) differ from those described by Alver & Furberg, and preclude any detailed comparison. In the context of plant metabolism, it is of interest that the conformation of the furanoid ring and the attached side groups shows many similarities to that of naturally occurring isocitric acid lactone (Glusker, Patterson, Love & Dornberg, 1963).

The calcium ion lies between two interlocking 5-keto-D-gluconate ions and is coordinated by O(1*a*), O(2), O(6)H, and H_2O, *i.e.* by four oxygen atoms, two hydroxyl groups and two water molecules, the eight oxygen atoms lying at the vertices of a regular triakistetrahedron. Calcium–oxygen distances vary between 2·39 Å and 2·47 Å. (Calcium coordination is shown in Fig. 4). Chelation of the calcium ion is shown by the formation of a planar ring system –C(1)–O(1*a*) → Ca ← O(2)–C(2)–, both of the oxygen atoms acting as donors. The lengths of the bonds C(2)–C(1) and C(1)–O(1*a*) are slightly shorter than those usually

Table 3. *Anisotropic thermal vibration parameters. Mean square vibration amplitude components* (Å²)

Calculated from the temperature factor

$$\exp\{-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{23}kl+b_{13}hl+b_{12}hk)\}$$

with

$$U_{11}=b_{11}/2\pi^2a^{*2};\quad U_{12}=b_{12}/4\pi^2a^*b^*;\quad etc.$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca	0·01799	0·00996	0·01293	0·00000	−0·00274	0·00000
O(1*a*)	0·02282	0·01451	0·01566	0·00398	−0·00672	−0·00404
O(1*b*)	0·02647	0·02387	0·01665	0·00336	−0·00025	−0·01261
O(2)	0·01266	0·00917	0·01884	0·00564	−0·00059	−0·00203
O(3)	0·02577	0·03433	0·02261	0·00808	0·01005	0·00745
O(4)	0·03861	0·01952	0·01719	0·00350	0·00108	−0·00284
O(5)	0·02455	0·02101	0·02087	0·00685	0·00746	0·00028
O(6)	0·03523	0·01952	0·02248	0·00031	−0·00064	−0·00647
C(1)	0·01735	0·01467	0·02037	−0·00454	0·00058	−0·00159
C(2)	0·01938	0·01184	0·01880	0·00092	−0·00348	−0·00476
C(3)	0·02011	0·02387	0·01897	0·00312	−0·00561	0·00007
C(4)	0·02731	0·01533	0·01058	0·00697	−0·00303	0·00133
C(5)	0·01916	0·01599	0·01488	0·00557	−0·00025	0·00165
C(6)	0·02759	0·01569	0·01810	0·00049	−0·00033	0·00313
H_2O	0·03038	0·02609	0·05542	−0·01757	0·02002	−0·00072

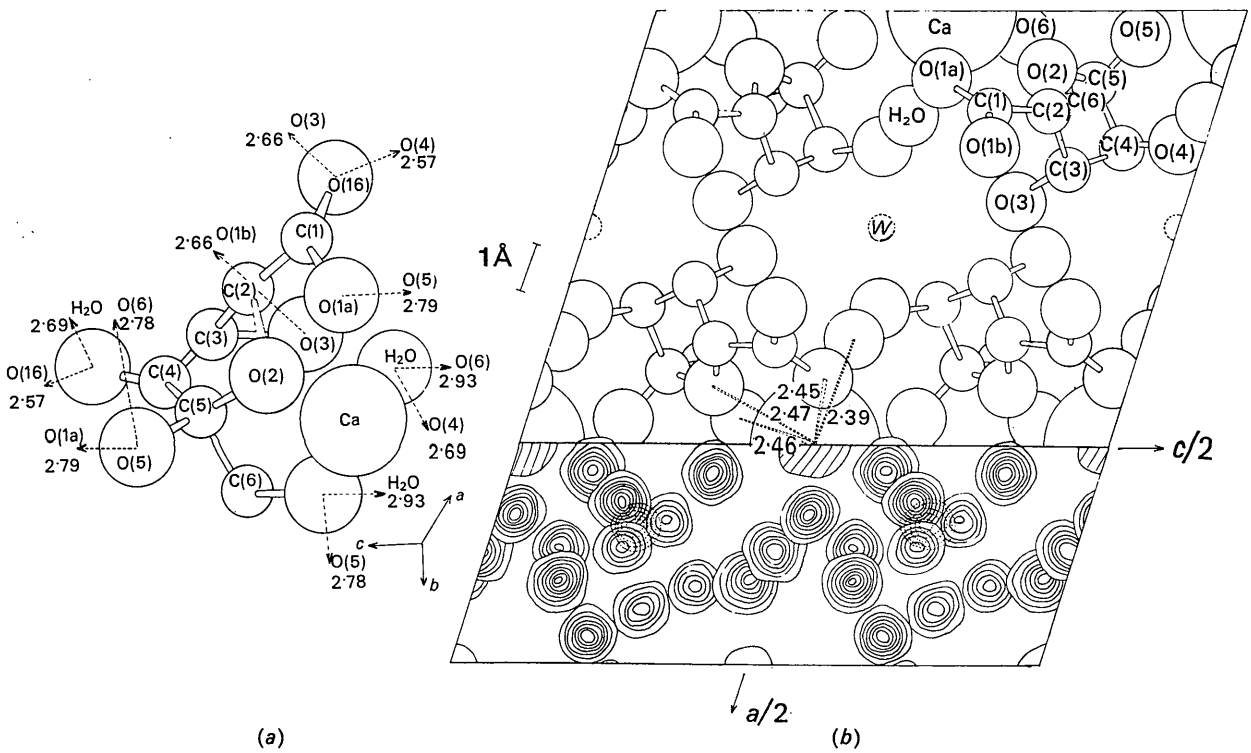


Fig. 3. (*a*) Asymmetric unit and interionic bonds (lengths in Å). (*b*) *b*-axis projection.

quoted for the C–C and C–OH bonds in carboxylic acids. The chelate structure appears to be further stabilized by the orientation of the bond C(6)–O(6), which completes the oxygen coordination of the calcium atom by forming a distorted ring system between –C(5)–O(2) · · · Ca · · · O(6)–C(6)–.

The calcium 5-ketogluconate molecules lie in well-defined sheets, consisting of calcium atoms sandwiched on either side by 5-ketogluconate ions. The bonding within these sheets is strong, through coordinate bonds between the calcium atoms and the carboxyl and glycosidic oxygen atoms, and through hydrogen bonds between adjacent ions. The layer-like nature of the structure, and the distribution of hydrogen bonds, is shown in Fig. 5. Hydrogen linkages are formed between O(1*a*) · · · HO(5) · · · HO(6) · · · H_2O · · · O(4)H · · · O(1*b*) · · · HO(3), providing a chain of bonds passing through the sheets of ions approximately midway between the calcium positions. The low decomposition temperature of 103 °C probably results from instability of the sheets caused by breakage of this chain, *e.g.* by removal of water. Lengths for the hydrogen bonds have been listed in Table 5.

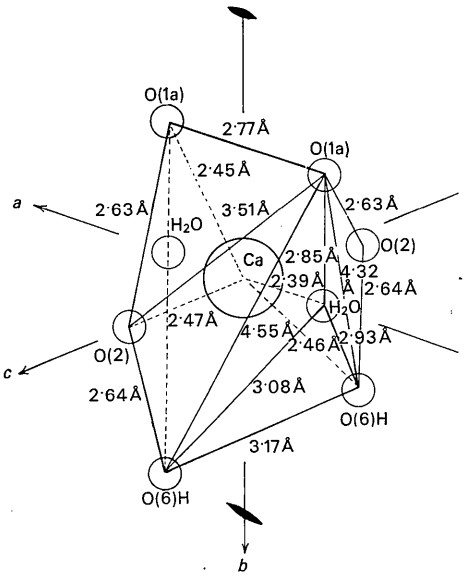


Fig. 4. Coordination of calcium ions by oxygen and hydroxyl groups.

Table 5. *Lengths of hydrogen bonds, with estimated standard deviations*

O(1*a*)–O(5)	2·78 ± 0·02 Å
O(1*b*)–O(3)	2·66
O(1*b*)–O(4)	2·57
O(5)–O(6)	2·78
H_2O–O(4)	2·69 ± 0·03 Å
H_2O–O(6)	2·93

Bonding between ionic sheets is relatively weak, and is mainly through the hydrogen bond O(1*b*) · · · HO(3), consistent with the cleavage properties of the material. However, the three-dimensional electron density map obtained after least-squares refinement exhibits a small peak (*W* in Table 2) on the diad axis at ($\frac{1}{2}$, −0·135, 0). This region appears void in Fig. 5, and in view of the divergence of reported water content for this compound may represent the position of a non-stoichiometric water molecule. Such a molecule completes the tetrahedral coordination around H_2O and would provide additional links, *via* H_2O, between the ionic sheets. It would not, however, itself be tetrahedrally coordinated by oxygen atoms, and the location of a water molecule at *W* could not be done without bond distortion.

Discussion

The cyclization of the 5-ketogluconate ion may be said to favour the formation of a chelate structure, since it brings oxygen atoms and hydroxyl groups into the proximity of the calcium ion. The possibility of ring

Table 4. *Intramolecular bond lengths and angles, with estimated standard deviations*

Bond length		Bond angle	
Ca–O(1*a*)	2·45 ± 0·02 Å	O(1*a*)–C(1)–O(1*b*)	124·7 ± 3·5°
Ca–O(2)	2·47	O(1*b*)–C(1)–C(2)	114·6
Ca–O(6)	2·46	O(1*a*)–C(1)–C(2)	120·8
Ca–H_2O	2·39	C(1)–C(2)–C(3)	115·7
		C(3)–C(2)–O(2)	103·2
O(1*a*)–C(1)	1·23 ± 0·03 Å	C(1)–C(2)–O(2)	109·9
O(1*b*)–C(1)	1·28	C(2)–C(3)–C(4)	101·2
C(1)–C(2)	1·49	C(2)–C(3)–O(3)	108·2
C(2)–C(3)	1·52	O(3)–C(3)–C(4)	110·8
C(3)–C(4)	1·51	C(3)–C(4)–C(5)	103·9
C(4)–C(5)	1·56	C(3)–C(4)–O(4)	106·7
C(5)–C(6)	1·51	O(4)–C(4)–C(5)	111·6
O(3)–C(3)	1·42	C(4)–C(5)–O(5)	113·4
O(4)–C(4)	1·41	C(4)–C(5)–C(6)	113·2
O(5)–C(5)	1·39	C(4)–C(5)–O(2)	104·5
O(6)–C(6)	1·44	O(5)–C(5)–O(2)	104·9
O(2)–C(2)	1·45	O(2)–C(5)–C(6)	108·8
O(2)–C(5)	1·44	O(5)–C(5)–C(6)	111·3
		C(5)–O(2)–C(2)	110·0
		C(5)–C(6)–O(6)	109·3

closure in calcium sequestrants is therefore of particular interest in connection with the study, now being undertaken, of calcium 2-ketogluconate. It would appear, on this basis, that the tendency for 2-ketogluconic acid to form chelates may also be assisted by lactolization; on the other hand, Littleton has shown that sodium gluconate, which is moderately effective as a calcium sequestrant, should possess a straight-chain organic ion, a ring arrangement being possible only after bond rotation.

Calcium 2-ketogluconate has been found, during preliminary investigation, to crystallize with the space group $P2_12_12_1$ with four molecules (of composition $Ca(C_6H_9O_7)_2 \cdot 3H_2O$) per unit cell. The structure cell dimensions are:

$a = 10{\cdot}43 \pm 0{\cdot}09$, $b = 18{\cdot}33 \pm 0{\cdot}06$, $c = 9{\cdot}50 \pm 0{\cdot}05$ Å.

The molecular volumes occupied in the solid materials by calcium 2-ketogluconate, by calcium 5-ketogluconate, and by rubidium gluconate (Littleton) are almost equal when allowance is made for the volume of the metallic ions. On this basis both straight-chain and ring configurations are possible for the 2-ketogluconate ion. However, the infrared absorption spectrum of crystalline calcium 2-ketogluconate, like that of calcium 5-ketogluconate, shows no evidence of the presence in the ion of a ketone group, indicating that for both compounds a chain configuration is unlikely.

In the 5-ketogluconate ion ring closure can occur only between the ketone group on C(5) and the hydroxyl group at C(2). If, as in the 2-ketogluconate ion, the ketone group is situated at C(2), there are two alternative sites for possible ring closure *viz.* the hydroxyl group at C(5), which would result in a five-membered ring, or the hydroxyl group at C(6), yielding a six-membered ring; such structures would favour the formation of chelate bonds. The three-dimensional X-ray analysis of this crystal is now in progress.

We are pleased to acknowledge the help afforded by the late Dr R. B. Duff, of the Macaulay Institute of Soil Research, Aberdeen, in providing samples of calcium 5-ketogluconate and calcium 2-ketogluconate used in the present investigation, and by Drs M. Rosemeyer and M. J. Ferrier for discussion of the results obtained. One of us (A.A.B.) is indebted also to the Department of Scientific and Industrial Research for a maintenance grant which allowed him to take part in this work. We are much indebted to Drs O. S. Mills and J. S. Rollett for the use of their crystallographic programs.

References

ALVER, E. & FURBERG, S. (1959). *Acta Chem. Scand.* **13**, 910.

BEEVERS, C. A. & COCHRAN, W. (1947). *Proc. Roy. Soc.* A, **190**, 257.

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.

BERNHAUER, K. & KNOBLOCH, K. (1940). *Biochem. Z.* **303**, 308.

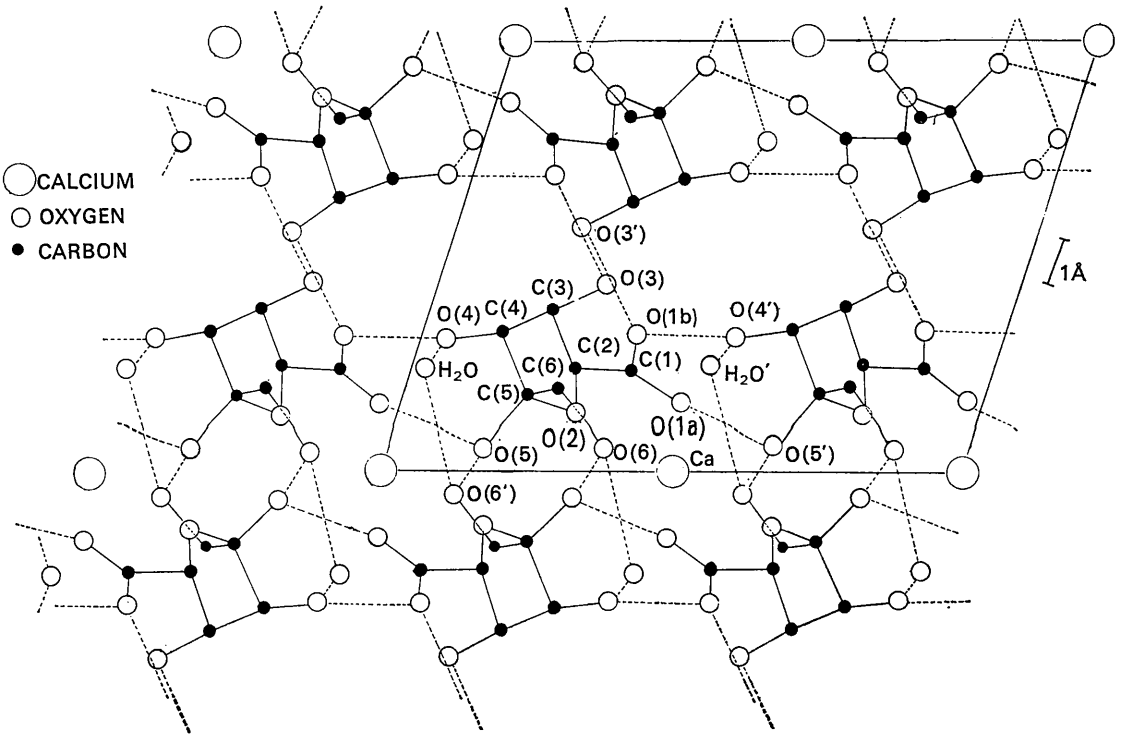


Fig. 5. *b*-axis projection showing distribution of hydrogen bonds (dotted lines). Bond lengths are listed in Tables 4 and 5.

COCHRAN, W. (1948). *J. Sci. Instrum.* **25**, 253.
DUFF, R. B. & WEBLEY, D. M. (1959). *Chemistry & Industry*, p. 1376.
FURBERG, S. (1950). *Acta Cryst.* **3**, 325.
GLUSKER, J. P., PATTERSON, A. L., LOVE, W. E. & DORNBERG, M. L. (1963). *Acta Cryst.* **16**, 1102.
JAMES, R. W. & BRINDLEY, J. (1931). *Phil. Mag.* (7), **12**, 81.
KILIANI, H. (1922). *Ber. dtsch chem. Ges.* **55**, 2817.
LITTLETON, C. D. (1953). *Acta Cryst.* **6**, 775.
MEHLTRETTER, C. L., ALEXANDER, B. H. & RIST, C. E. (1953). *Ind. Engng Chem.* **45**, 2782.
MILLS, O. S. & ROLLETT, J. S. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p .107. London: Pergamon Press.
PRESCOTT, F. J., SHAW, J. K., BILELLO, J. P. & CRAGWALL, G. O. (1953). *Ind. Engng Chem.* **45**, 338.
STUBBS, J. J., LOCKWOOD, L. B., ROE, E. T., TOBENKIN, R. & WARD, G. E. (1940). *Ind. Engng Chem.* **33**, 1626.
WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.

Acta Cryst. (1965). **19**, 111

The Crystal Structure of Deoxyadenosine Monohydrate

BY D. G. WATSON*
Cavendish Laboratory, Cambridge, England
and the Department of Biological Structure, University of Washington, Seattle, Washington, U.S.A.

AND D. J. SUTOR† AND P. TOLLIN‡
Cavendish Laboratory, Cambridge, England

(*Received* 5 *October* 1964)

Deoxyadenosine crystallizes as the monohydrate in the monoclinic space group $P2_1$ with two molecules in a unit cell of dimensions: $a=16{\cdot}060\pm0{\cdot}007$, $b=7{\cdot}866\pm0{\cdot}003$, $c=4{\cdot}700\pm0{\cdot}002$ Å, $\beta=96°\ 4'\pm1'$. Angular coordinates of the plane of the adenine group and atom C(1′) of the glycosidic bond were found by integrating the Patterson function, and used in computing a superposition function from which the translational coordinates of the group were determined. The remaining atoms including the hydrogen atoms were located in three-dimensional Fourier syntheses and difference syntheses. The coordinates of the non-hydrogen atoms and the thermal parameters were refined by the full-matrix least-squares method. The final R index is 7·8 % and the standard deviations in the bond lengths and angles are about 0·01 Å and 1° respectively.

The bond lengths and angles in the base are closely similar to those in other adenine compounds. In the sugar, the only significant differences between these molecular dimensions and those in other compounds containing D-ribofuranose or 2-deoxy-D-ribofuranose occur in the exocyclic angles at C(3′). The differences are in accordance with steric hindrance between O(2′) and O(3′) in D-ribofuranose. The adenine group is planar, but the carbon atom of the glycosidic bond is displaced by 0·220 Å from this plane. The sugar ring is puckered with C(3′) displaced by 0·552 Å from the plane of the other four ring atoms so that the atom O(3′) is 1·970 Å from the plane. The dihedral angle between the sugar and base planes is 70°, and the conformation of the molecule is *anti* with the torsion angle $\varphi_{CN}=-3°$.

The packing in the crystal is determined by hydrogen bonds in which all available groups participate. The outstanding features of the system are infinite chains of N–H · · · N bonds between bases related by a screw axis, and a distorted trigonal arrangement of O–H · · · O bonds formed by the water molecule.

Introduction

The molecular structures of biological molecules are thought to be closely related to their physiological functions. Probable structures for the deoxyribonucleic acid (DNA) and ribonucleic acid (RNA), which will help explain their essential part in protein synthesis and genetic replication, are investigated at present by the method of trial and error. The complexity of these molecules necessitates a knowledge of the molecular dimensions and of the conformation of the units comprising them. By imposing restrictions on these factors, a spatial arrangement of the molecule, compatible with the available X-ray data, is sought.

The crystal structures of many pyrimidine and purine bases and a few nucleosides and nucleotides have been published. This work has provided information on not only the molecular configuration of some of the units but also certain fairly characteristic features of the molecular packing which probably help govern the struc-

* Present address: Department of Biological Structure, University of Washington, Seattle, Washington, U.S.A.
† Present address: Birkbeck College Crystallography Laboratory, 21 Torrington Square, London W. C. 1, England.
‡ Present address: Physics Department, Queen's College, University of St. Andrews Dundee, Scotland.