International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
Murrell, W. G. & Warth, A. D. (1965). *Spores*, III, edited by Campbell, L. L. & Halvorson, H. O., p. 1. Ann Arbor: Amer. Soc. Microbiology.
Oyama, J., Nakamura, N. & Tanabe, O. (1960). *Bull. Agr. Chem. Soc. Japan*, **24**, 743.
Powell, J. F. (1953). *Biochem. J.* **54**, 205.
Shima, M. (1955). *Sanshi Shikenjo Hokoku*, **14**, 427.
Strahs, G. (1965). Thesis, Univ. of Illinois.
Strahs, G. & Dickerson, R. E. (1964). Abstracts A.C.A. Bozeman Meeting, E-5, p. 45.
Strahs, G. & Dickerson, R. E. (1965). *Spore Newsletter*, **2**, 30.
Sutor, D. J. (1963). *J. Chem. Soc.* p. 1105.
Trueblood, K. N., Horn, P. & Luzzati, V. (1961). *Acta Cryst.* **14**, 965.
Udo, S. (1936). *J. Agr. Chem. Soc. Japan*, **12**, 386.

Acta Cryst. (1968). B**24**, 578

X-ray Crystal Analysis of the Substrates of Aconitase.
VIII. The Structure and Absolute Configuration of Potassium Dihydrogen Isocitrate Isolated from *Bryophyllum Calycinum*[*]

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Anhydrous potassium dihydrogen isocitrate, prepared from the isomer of isocitric acid which is active in the tricarboxylic acid cycle, crystallizes in the space group $P2_12_12_1$ with four formula units, $K(C_6O_7H_7)$ in the unit cell of dimensions $a = 12\cdot013$, $b = 13\cdot145$ and $c = 5\cdot159$ Å. Two complete sets of three-dimensional data were collected, one set with Cu $K\alpha$ radiation (Mo $K\alpha$ for $hk0$ and $h0l$ reflections) and the other set with Cr $K\alpha$ radiation. The structure was solved by comparing the $|F|^2$ map for the Cu–Mo data with the P_s map for the Cr data. The final R values are 8·3% for the Cu–Mo data and 2·3% for the (more limited) Cr data. The absolute configuration of the biologically active isomer, (+)-isocitric acid, is (1*R* : 2*S*)-1-hydroxy-1,2,3-propanetricarboxylic acid. The ion is fully extended and there is slight disorder in the position of one carboxylic acid group. The central carboxyl group is the one that is ionized in this crystalline form. The ion forms a tridentate chelate with one potassium ion and a bidentate chelate with another.

Introduction

The isomer of isocitric acid present in the leaves of the succulent plant *Bryophyllum calycinum* is a substrate of the enzyme aconitase in the tricarboxylic acid cycle. The relative and absolute configurations of this isomer have already been determined crystallographically from a study of the potassium and rubidium salts of its lactone (Glusker, Patterson, Love & Dornberg, 1963; Patterson, Johnson, van der Helm & Minkin, 1962). When crystalline salts of the acid itself became available the present structure analysis was initiated to determine the shape, the mode of ionization and the packing of the isocitrate ion.

Experimental

Needle-like crystals of potassium and rubidium dihydrogen isocitrate were prepared for us from the leaves of *Bryophyllum calycinum* by Dr H. B. Vickery and Dr D. G. Wilson of the Connecticut Agricultural Experiment Station. These are isomorphous, crystallizing in the space group $P2_12_12_1$ (systematic absences $h00$ if h is odd, $0k0$ if k is odd, $00l$ if l is odd) with four metal ions and four isocitrate ions ($C_6O_7H_7^-$) in the unit cell. There is no water of crystallization. The unit-cell dimensions of the rubidium salt were measured from precession photographs. Those of the potassium salt were measured from high angle reflections on the General Electric XRD-5 diffractometer using both copper and chromium radiation. These values, and the densities measured by flotation, are given in Table 1. The structure determination was done on the potassium salt alone.

Data collection

X-ray intensity measurements were made with crystals which were ground as spheres in order to simplify the

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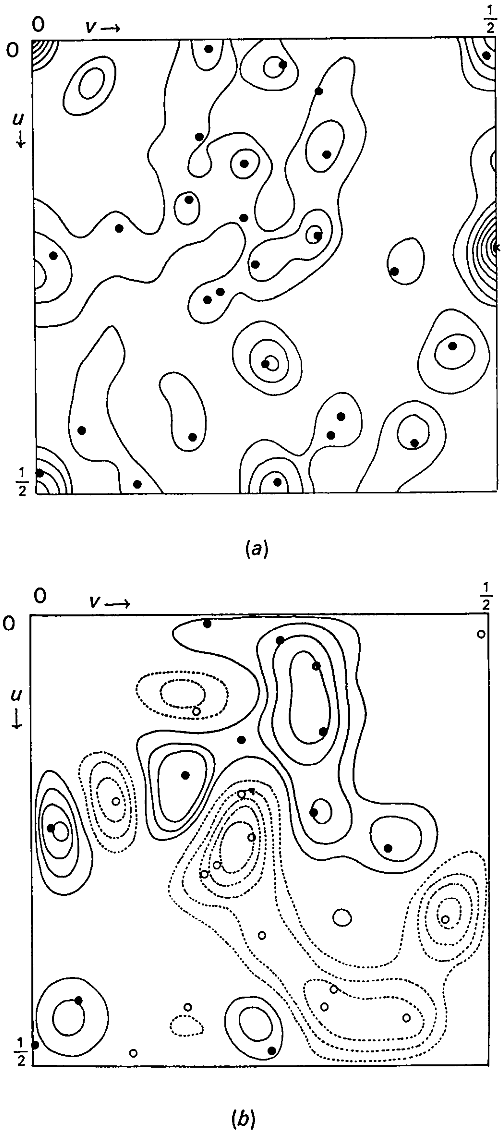


Fig. 1. Comparison of $|F|^2$ and P_s maps. (*a*) $|F|^2$ map $[P(u,v,w)]$ for Cu–Mo data. Section $w=0{\cdot}150$. Contour interval arbitrary and equal. K–O and K–C vectors: filled circles; K–K vector: cross. (*b*) P_s map $[P_s(u,v,w)]$ for Cr data. Section $w=0{\cdot}150$. Contour interval arbitrary and equal. K → O and K → C vectors (positive): filled circles; O → K and C → K vectors (negative): open circles. Contours: positive – solid lines; negative – broken lines (zero contour omitted). (Vectors close to the mirror planes in the $|F|^2$ map do not appear in the P_s synthesis owing to the antisymmetry of the P_s function with respect to these planes).

absorption geometry. The crystal used with Mo radiation had a radius of 0·06 mm, while the crystals used for the Cu and Cr data collection had radii of approximately 0·13 mm. Complete three-dimensional data ($2\theta < 161{\cdot}5°$) for the potassium salt were collected on the diffractometer with chromium $K\alpha$ radiation. The anomalous dispersion corrections (*International Tables for X-ray Crystallography*, 1962*b*) for potassium ions are $\Delta f'=0{\cdot}0$ and $\Delta f''=2{\cdot}2$ for chromium radiation. A measurement was therefore made on each hkl, $\bar{h}k\bar{l}$, $\bar{h}kl$ and $hk\bar{l}$ reflection. The four measurements were made consecutively (so that they were subject to similar instrumental uncertainties) before proceeding to the next set. Averages of the values for the crystallographically equivalent reflections (*i.e.* $hkl=\bar{h}k\bar{l}$ and $\bar{h}kl=hk\bar{l}$) resulted in 551 data (to be referred to as 'Cr data'), of which 16 were below the threshold value for an observed reflection. Of those observed 191 were for hkl, 191 for $\bar{h}kl$ and 153 for reflections with one or more zero indices. An intermeasurement factor

$$\Sigma\ ||F_{\rm obs}(hkl)| - |F_{\rm obs}(\bar{h}k\bar{l})|| + ||F_{\rm obs}(\bar{h}kl)| - |F_{\rm obs}(hk\bar{l})||/2|F_{\rm obs}|{\rm av.}$$

was 2·4% for those reflections with non-zero indices.

Three-dimensional data (hkl reflections only) were collected with copper $K\alpha$ radiation ($\Delta f'=0{\cdot}3$, $\Delta f''=1{\cdot}1$) using an integrating Weissenberg camera. The intensities were measured with a Nonius densitometer. A General Electric XRD-5 diffractometer was used with copper $K\alpha$ radiation to remeasure all reflections with $|F|$ greater than 25·0 and to measure reflections geometrically inaccessible on the films. For the $hk0$ and $h0l$ reciprocal net planes Mo $K\alpha$ radiation was used. Data collected with copper radiation and with molybdenum radiation were scaled together. These combined data will be referred to as 'Cu–Mo data' and consist of 1356 reflections, of which 602 were measured on the diffractometer with Mo $K\alpha$ radiation, 85 were Cu $K\alpha$ diffractometer measurements, 394 were Weissenberg measurements using Cu $K\alpha$ radiation, and 275 were below the threshold of the technique of measurement.

The data were corrected for absorption and Lorentz and polarization factors. (Since the linear absorption coefficient μ for Mo $K\alpha$ radiation (6·96 cm^{-1}) is very much less than for Cu $K\alpha$ (58·9 cm^{-1}) and Cr $K\alpha$ (178 cm^{-1}) no absorption correction was applied to the Mo data.) The Cr data and the Cu–Mo data were kept separate at all times.

Table 1. *Cell dimensions and densities*

	a	*b*	*c*	Density (obs.)	Density (calc.)
K salt	12·013 Å	13·145 Å	5·159 Å	1·89 g.cm^{-3}	1·877 g.cm^{-3}
Rb salt	12·045	13·375	5·221	2·19	2·184

Estimated standard deviations: axial lengths K salt 0·05%
Rb salt 0·13%
observed densities 1%

Wavelengths used (Å). K salt: Cu $K\alpha_1$, 1·5405; Cu $K\alpha_2$, 1·5443; Cr $K\alpha_1$, 2·2896
Rb salt: Cu $K\alpha$, 1·5418

Determination of a trial structure

The position of the potassium ion was found from the sharpened $|F|^2$ synthesis from the Cu–Mo data. The y coordinate of the potassium ion is nearly zero and this made a direct solution of the $|F|^2$ map from the heavy atom position difficult. For this reason the P_c and P_s functions (Okaya & Pepinsky, 1956) were computed from the Cr data, for which the effect of anomalous dispersion is appreciable. The structure was deter-

Table 2. *Parameters of potassium, oxygen and carbon atoms for potassium dihydrogen isocitrate*

Positional parameters are expressed as fractions of cell edges. Anisotropic temperature factors are expressed as

$$\exp\{-(h^2b^{11}+k^2b^{22}+l^2b^{33}+2hkb^{12}+2hlb^{13}+2klb^{23})\}.$$

For a given atom, values on the first line are for the Cu–Mo data, on the second line for Cr data, and on the third line, in parentheses, the standard deviations (for the last decimal place given) for Cu–Mo data and Cr data respectively.

	x	y	z	b^{11}	b^{22}	b^{33}	b^{12}	b^{13}	b^{23}
K	0·3830	0·0055	0·6781	0·0066	0·0034	0·0397	0·0017	−0·0044	−0·0033
	0·3830	0·0051	0·6780	0·0076	0·0039	0·0433	0·0019	−0·0047	−0·0033
	(2)(1)	(1)(1)	(4)(3)	(1)(2)	(1)(2)	(9)(12)	(1)(1)	(3)(3)	(2)(3)
O(1)	0·1295	0·2520	0·8658	0·0053	0·0030	0·0357	0·0000	0·0062	−0·0003
	0·1299	0·2523	0·8635	0·0058	0·0035	0·0346	0·0004	0·0070	0·0004
	(5)(5)	(4)(4)	(13)(13)	(4)(4)	(3)(5)	(26)(24)	(3)(4)	(8)(9)	(7)(11)
O(2)	0·1716	0·0950	0·7347	0·0043	0·0031	0·0301	−0·0001	0·0024	0·0005
	0·1719	0·0954	0·7334	0·0062	0·0022	0·0379	0·0003	0·0016	0·0004
	(5)(4)	(4)(5)	(12)(9)	(3)(5)	(3)(5)	(23)(29)	(2)(3)	(7)(8)	(6)(9)
O(3)	0·4551	0·5441	0·2935	0·0131	0·0028	0·0646	−0·0012	0·0169	0·0014
	0·4534	0·5444	0·2910	0·0158	0·0033	0·0672	−0·0014	0·0171	0·0005
	(8)(7)	(5)(7)	(21)(17)	(8)(8)	(3)(5)	(46)(45)	(4)(5)	(17)(16)	(11)(15)
O(4)	0·3727	0·5296	0·6696	0·0079	0·0038	0·0393	−0·0002	0·0043	−0·0012
	0·3724	0·5297	0·6693	0·0105	0·0044	0·0404	0·0002	0·0043	−0·0021
	(6)(5)	(5)(5)	(15)(14)	(5)(5)	(3)(4)	(32)(35)	(3)(4)	(11)(11)	(8)(11)
O(5)	0·5096	0·3229	0·7832	0·0038	0·0035	0·0280	−0·0004	−0·0014	0·0018
	0·5099	0·3235	0·7860	0·0041	0·0035	0·0294	−0·0008	−0·0024	0·0007
	(4)(5)	(4)(4)	(12)(10)	(3)(5)	(3)(3)	(21)(23)	(2)(3)	(7)(8)	(7)(8)
O(6)	0·3977	0·1970	0·8995	0·0051	0·0026	0·0227	−0·0002	−0·0007	0·0017
	0·3971	0·1967	0·8998	0·0054	0·0035	0·0223	−0·0002	0·0005	0·0017
	(5)(4)	(4)(5)	(11)(11)	(4)(4)	(2)(4)	(19)(24)	(3)(4)	(7)(9)	(6)(10)
O(7)	0·3000	0·1596	0·3582	0·0063	0·0033	0·0184	0·0006	0·0027	−0·0002
	0·2995	0·1599	0·3596	0·0070	0·0050	0·0224	0·0006	0·0035	−0·0002
	(5)(5)	(4)(4)	(11)(12)	(4)(5)	(3)(4)	(20)(27)	(3)(4)	(8)(10)	(6)(11)
C(1)	0·1799	0·1877	0·7151	0·0028	0·0028	0·0212	0·0000	0·0001	0·0013
	0·1807	0·1859	0·7150	0·0033	0·0035	0·0243	−0·0001	−0·0015	−0·0019
	(5)(6)	(5)(8)	(14)(16)	(3)(6)	(3)(8)	(24)(40)	(3)(6)	(8)(14)	(8)(17)
C(2)	0·2464	0·2382	0·4987	0·0037	0·0029	0·0197	0·0001	0·0005	0·0009
	0·2471	0·2391	0·5001	0·0039	0·0033	0·0266	0·0009	0·0024	−0·0006
	(6)(7)	(6)(6)	(16)(16)	(4)(6)	(3)(6)	(22)(29)	(3)(6)	(8)(14)	(8)(14)
C(3)	0·3276	0·3197	0·6014	0·0028	0·0034	0·0184	0·0001	−0·0008	0·0004
	0·3278	0·3197	0·5998	0·0052	0·0029	0·0222	−0·0004	−0·0004	−0·0007
	(5)(6)	(5)(6)	(15)(16)	(4)(7)	(4)(6)	(22)(40)	(3)(6)	(8)(16)	(8)(15)
C(4)	0·3714	0·3861	0·3821	0·0045	0·0031	0·0244	−0·0003	−0·0002	0·0013
	0·3727	0·3865	0·3810	0·0052	0·0042	0·0213	−0·0002	−0·0004	0·0018
	(6)(8)	(6)(7)	(16)(17)	(5)(8)	(3)(8)	(28)(38)	(3)(6)	(10)(15)	(9)(15)
C(5)	0·3994	0·4933	0·4656	0·0046	0·0027	0·0434	0·0005	0·0019	0·0009
	0·3985	0·4940	0·4688	0·0062	0·0030	0·0359	0·0000	0·0031	0·0020
	(7)(7)	(6)(7)	(19)(23)	(5)(8)	(4)(8)	(40)(49)	(4)(7)	(11)(18)	(10)(21)
C(6)	0·4192	0·2751	0·7698	0·0034	0·0027	0·0177	0·0000	−0·0006	−0·0009
	0·4183	0·2751	0·7702	0·0049	0·0038	0·0123	0·0005	−0·0001	−0·0014
	(5)(7)	(5)(8)	(14)(15)	(4)(8)	(3)(7)	(23)(32)	(3)(7)	(8)(14)	(7)(15)

mined by obtaining directions for the vectors in the $|F|^2$ map (prepared from the Cu–Mo data) from the signs of the corresponding vectors in the P_s map (from the Cr data). This is shown by a comparison of similar sections in Fig. 1. A comparison of the vector environment of each potassium–potassium vector at distances from 2·7–3·4 Å gave the positions and the absolute configuration of the oxygen atoms around the potassium ions. By building a model it was possible to postulate carbon atom positions and check vectors for these on the $|F|^2$ map. All but one of the oxygen atoms [O(1)] is in contact with a potassium ion. The final model gave vectors which agreed well with the $|F|^2$ and P_s maps as shown in Fig. 1. Since the resolution of the $|F|^2$ map from the Cu–Mo data was better than the resolution of the P_c and P_s maps from the Cr data the $|F|^2$ map was used to derive the atomic coordinates.

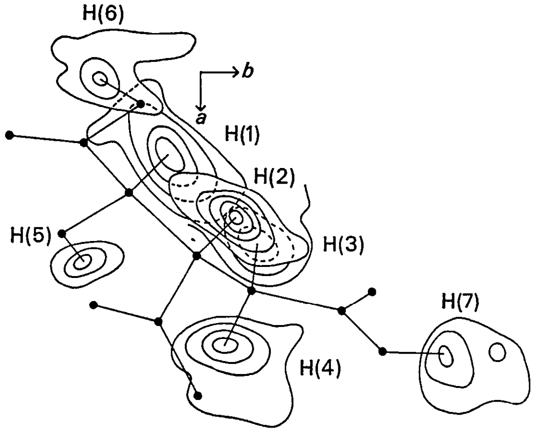


Fig. 2. Location of hydrogen atoms from a three-dimensional difference Fourier map. Composite map: first contour 0·1 e.Å^{-3}; interval 0·1 e.Å^{-3}.

Refinement of the structure

(*a*) Cu–Mo *data*

The Cu–Mo data were corrected for anomalous dispersion using the formula given by Patterson (1963). The values of $|F_o|$ so obtained are independent of anomalous dispersion effects and were refined with a block-diagonal least-squares program. (Matrices for each atom were 3×3 for positional parameters, 6×6 for anisotropic and 1×1 for isotropic temperature factors.) The weights assigned were $(1/|F_o|)^2$ for observed reflections and $1/(3|F_{\min}|)^2$ for unobserved reflections. Reflections for which both $|F_o|$ and $|F_c|$ were small, and low angle reflections with large negative

Table 3. *Parameters of hydrogen atoms for potassium dihydrogen isocitrate*

Positional parameters are expressed as fractions of cell edges. Isotropic temperature factors for the Cu–Mo data are expressed in the form $\exp(-B\sin^2\theta/\lambda^2)$ and are given in Å^2. For the Cr data the hydrogen atoms were given the anisotropic temperature factors of the atoms to which they are attached (these were not refined) and an occupancy factor which was refined.

For a given atom, values on the first line are for the Cu–Mo data, on the second line for Cr data, and on the third line, in parentheses, the standard deviations (for the last decimal place given) for Cu–Mo data and Cr data respectively.

Parameters for H(7) which are marked with an asterisk were obtained from the final difference map with this atom excluded from the structure factor calculation. No temperature factor is given for this atom and the positional parameters were not refined further.

	x	*y*	*z*	*B*	Attached to:	Occupancy factor
H(1)	0·199	0·294	0·364	4·4	C(2)	
	0·184	0·278	0·389			1·06
	(11)(8)	(11)(7)	(29)(17)	(2·7)		(16)
H(2)	0·277	0·361	0·740	1·0	C(3)	
	0·290	0·371	0·716			0·78
	(6)(10)	(6)(10)	(16)(23)	(1·4)		(17)
H(3)	0·341	0·401	0·238	3·3	C(4)	
	0·313	0·400	0·229			0·85
	(10)(10)	(8)(8)	(22)(22)	(2·3)		(17)
H(4)	0·442	0·366	0·288	5·6	C(4)	
	0·436	0·353	0·276			0·95
	(13)(10)	(12)(7)	(31)(19)	(3·2)		(18)
H(5)	0·330	0·172	0·234	2·9	O(7)	
	0·347	0·173	0·240			0·86
	(9)(10)	(8)(8)	(21)(27)	(2·1)		(19)
H(6)	0·088	0·204	1·031	5·2	O(1)	
	0·083	0·219	0·978			1·32
	(12)(9)	(11)(7)	(27)(19)	(3·4)		(22)
H(7)	0·452*	0·604*	0·257*	*	O(3)	
	0·465	0·603	0·262			0·95
	(10)	(10)	(23)			(21)

Table 4. *Observed and calculated structure factors* (Cu–Mo *data*)

The observed data are corrected for extinction and anomalous dispersion. An asterisk indicates that the reflection was too weak for measurement; the value listed corresponds to an intensity of one-third the threshold intensity of the technique of measurement used. For each reflection the observed and calculated structure factors are given (in electrons) followed by the phase angle (°) Parameters for H(7) were omitted from the calculation of structure factors (see text).

H	OBS	CALC	ALPHA
(H,0,0)			
2	6.9	7.9	180
4	120.5	115.5	180
6	7.5	8.5	0
8	34.7	35.9	0
10	25.3	22.2	0
12	1.2*	0.2	0
14	16.6	15.0	180
16	12.2	10.5	0
18	1.2*	2.6	0
20	1.3*	3.8	160
(H,1,0)			
1	28.2	30.8	90
2	18.3	22.4	0
3	15.7	16.2	270
4	11.3	12.9	0
5	24.5	27.3	270
6	0.9*	0.1	0
7	5.9	6.2	270
8	28.8	28.5	180
9	7.0	5.9	270
10	9.3	9.4	180
11	10.5	11.3	90
12	1.4*	1.8	0
13	4.2	5.0	90
14	1.2*	0.8	0
15	6.2	5.7	270
16	1.8*	0.6	0
17	1.9*	0.3	90
18	6.0	4.8	180
19	2.0*	3.1	90
20	2.1*	0.2	0
21	2.2*	1.0	90
(H,2,0)			
0	5.9	8.7	180
1	22.0	28.2	90
2	38.4	38.8	0
3	16.8	16.5	270
4	56.2	60.5	180
5	28.7	28.3	90
6	9.9	10.3	180
7	23.7	26.7	90
8	19.4	19.6	0
9	12.2	13.9	270
10	2.3	1.8	0
11	9.3	9.7	90
12	21.8	21.1	180
13	6.5	6.4	90
14	4.0	3.5	180
15	1.2*	1.8	270
16	1.8*	1.7	180
17	7.4	6.6	90
18	1.9*	4.7	0
19	4.7	3.3	270
20	2.2*	0.6	0
21	2.2*	1.5	270
(H,3,0)			
1	24.1	25.6	270
2	11.1	11.5	180
3	11.5	11.8	90
4	15.6	14.5	180
5	23.4	25.6	270
6	16.8	17.9	180
7	23.9	26.1	270
8	1.0*	3.2	180
9	9.6	10.9	90
10	17.9	19.6	0
11	1.2*	2.0	270
12	1.3*	1.9	180
13	9.7	8.4	270
14	7.7	6.8	180
15	7.0	4.5	270
16	1.8*	1.1	0
17	1.9*	0.9	270
18	2.0*	2.0	0
19	4.2	3.0	90
20	2.2*	0.7	180
21	2.2*	2.3	270
(H,4,0)			
0	103.1	97.2	0
1	44.7	45.4	270
2	25.3	28.5	0
3	33.5	35.2	270
4	67.1	68.4	180
5	12.9	12.3	270
6	46.6	49.3	180
7	12.6	12.2	270
8	42.8	42.9	0
9	4.6	4.0	90
10	5.5	4.8	0
11	5.3	5.4	270
12	7.8	8.2	180
13	5.1	4.1	270
14	8.4	6.9	180
15	1.8*	0.1	90
16	1.7*	3.3	0
17	1.9*	4.9	270
18	2.0*	1.4	180
19	2.1*	2.7	90
20	2.2*	0.6	[illegible]
21	2.2*	0.6	90
(H,5,0)			
1	27.4	30.6	90
2	52.2	52.9	180
3	27.1	28.6	90
4	22.3	23.6	0
5	9.4	7.4	270
6	1.2*	0.2	0
7	29.8	32.1	270
8	8.1	8.9	180
9	11.5	13.1	90
10	9.3	9.9	180
11	23.5	22.6	90
12	6.5	6.2	0
13	1.6*	3.6	270
14	7.9	7.5	0
15	8.2	7.5	270
16	1.9*	1.0	0
17	1.9*	4.2	90
18	2.0*	1.0	180
19	2.1*	1.3	90
20	2.2*	1.0	0
21	2.2*	1.8	90
(H,6,0)			
0	59.1	67.8	0
1	36.8	37.8	270
2	16.2	15.9	0
3	16.3	14.9	90
4	19.3	22.4	180
5	29.0	31.4	90
6	6.0	6.3	0
7	10.4	9.7	270
8	11.1	11.6	0
9	10.4	10.8	270
10	28.6	28.4	0
11	9.5	9.7	90
12	7.9	7.3	180
13	7.4	7.6	90
14	7.4	6.8	180
15	1.8*	0.9	90
16	1.8*	1.5	0
17	2.0*	0.3	270
18	8.2	5.9	0
19	2.1*	2.6	270
20	2.2*	0.0	90
21	2.2*	0.1	90
(H,7,0)			
1	9.9	11.4	90
2	20.3	18.3	0
3	16.1	17.3	90
4	22.7	23.6	180
5	2.0	4.0	270
6	8.9	10.2	180
7	6.1	6.6	270
8	12.1	12.2	180
9	1.5*	1.3	90
10	7.3	6.7	180
11	10.1	9.3	90
12	4.7	5.1	0
13	10.0	9.3	270
14	1.1*	1.9	0
15	1.8*	0.0	90
16	8.7	7.9	180
17	2.0*	2.7	90
18	2.1*	3.0	180
19	2.1*	1.5	90
20	2.2*	1.3	0
(H,8,0)			
0	22.3	23.8	0
1	28.8	31.5	270
2	10.5	10.6	180
3	28.4	28.7	90
4	41.8	43.7	180
5	2.3	2.9	90
6	24.6	26.2	180
7	6.1	6.8	90
8	33.6	34.4	0
9	1.2*	2.6	90
10	3.3	3.6	180
11	1.3*	0.2	90
12	16.4	15.7	180
13	1.7*	2.6	90
14	1.8*	0.4	0
15	1.9*	0.2	270
16	4.3	3.6	0
17	2.0*	0.3	90
18	2.1*	2.3	180
19	2.2*	2.0	90
20	2.2*	0.4	0
(H,9,0)			
1	10.8	11.5	90
2	8.8	9.1	180
3	10.7	11.0	90
4	10.0	11.0	180
5	8.7	9.4	270
6	13.9	15.1	0
7	7.7	8.3	270
8	1.0*	3.0	180
9	12.1	12.9	90
10	8.3	8.6	180
11	1.1*	0.2	270
12	8.1	8.0	0
13	1.8*	0.9	90
14	1.8*	2.4	0
15	11.6	9.2	270
16	2.0*	1.3	180
17	2.1*	3.3	270
18	1.3*	0.8	0
19	2.1*	2.5	90
20	2.2*	1.2	0
(H,10,0)			
0	26.5	28.3	0
1	16.9	17.0	270
2	0.6*	2.6	0
3	0.5*	1.8	90
4	36.4	38.4	180
5	7.9	8.7	270
6	0.7*	1.4	0
7	15.8	14.8	270
8	7.5	8.3	0
9	1.2*	0.5	270
10	13.7	12.7	0
11	5.6	6.3	270
12	1.7*	0.8	0
13	1.8*	3.3	90
14	10.8	9.2	180
15	1.1*	3.5	90
16	2.0*	0.3	0
17	7.0	5.5	270
18	5.3	4.6	0
19	2.2*	1.6	270
(H,11,0)			
1	24.6	26.3	90
3	28.9	31.0	90
4	17.9	18.5	0
5	8.8	10.1	270
6	21.0	21.0	180
7	0.5*	1.6	270
8	8.8	9.5	180
9	1.2*	1.9	90
10	10.1	8.8	0
11	11.3	9.8	90
12	1.7*	3.4	0
13	1.8*	0.6	270
14	1.9*	0.3	0
15	1.9*	2.1	270
16	2.0*	2.2	180
17	2.1*	2.9	90
18	2.2*	0.0	90
19	4.0	3.4	90
(H,12,0)			
0	27.5	28.7	0
1	0.4*	0.7	270
2	11.5	11.4	180
3	6.3	7.2	270
4	10.4	12.0	180
5	26.1	26.0	90
6	5.9	6.2	0
7	7.1	7.8	90
8	11.1	11.7	0
9	12.5	11.8	270
10	6.6	5.6	0
11	1.8*	2.2	90
12	0.9*	1.2	180
13	1.9*	0.2	270
14	1.9*	3.7	180
15	2.0*	1.3	90
16	5.8	4.2	0
17	2.2*	3.1	90
18	1.3*	1.7	0
(H,13,0)			
1	16.1	16.4	90
2	0.9*	2.7	180
3	0.7*	1.2	90
4	3.9	4.8	0
5	6.4	7.8	270
6	1.3*	1.4	0
7	5.0	5.1	270
8	7.0	7.0	180
9	14.8	14.4	90
10	1.8*	1.2	180
11	5.6	5.3	90
12	1.7*	3.4	0
13	8.1	7.6	270
14	2.0*	1.2	180
15	7.5	5.9	270
16	2.1*	3.3	180
17	2.2*	1.9	90
18	2.2*	2.7	180
(H,14,0)			
0	10.9	9.3	180
1	0.8*	2.3	90
2	3.7	2.2	0
3	9.1	8.1	90
4	9.6	10.1	180
5	1.3*	2.1	270
6	17.7	15.9	180
7	1.0*	2.7	270
8	3.2	3.4	0
9	5.0	4.6	270
10	6.2	6.0	0
11	2.9	1.5	90
12	4.4	5.5	180
13	6.7	6.0	90
14	1.3*	0.5	0
15	2.1*	1.9	270
16	2.2*	2.2	180
17	2.2*	1.2	270
(H,15,0)			
1	6.4	6.9	90
2	12.2	11.3	0
3	20.4	20.3	90
4	8.4	8.0	0
5	9.6	8.8	270
6	0.9*	1.0	0
7	8.9	9.7	270
8	7.4	6.8	180
9	0.9*	3.9	90
10	4.2	2.9	0
11	7.6	6.4	90
12	5.4	5.0	0
13	3.2	4.0	270
14	2.1*	0.0	90
15	1.3*	2.1	270
16	2.2*	0.3	0
(H,16,0)			
0	13.1	14.0	0
1	10.2	8.9	270
2	0.9*	1.3	0
3	6.6	4.8	90
4	12.1	12.5	180
5	6.3	6.8	90
6	0.9*	1.3	180
7	3.5	2.9	270
8	12.7	11.8	0
9	7.2	7.1	270
10	2.0*	2.3	0
11	4.1	4.1	270
12	1.1*	3.2	180
13	2.1*	0.0	90
14	4.2	4.2	180
15	2.2*	1.7	90
16	1.3*	3.2	0
(H,17,0)			
1	0.6*	1.6	90
2	4.9	4.3	0
3	1.8*	0.7	270
4	8.3	7.7	0
5	1.8*	0.0	90
6	5.1	4.1	180
7	5.7	4.8	270
8	1.8*	3.3	180
9	9.1	8.4	90
10	2.0*	1.4	0
11	2.0*	3.4	90
12	5.1	4.3	0
13	2.1*	2.0	270
14	2.2*	1.7	0
15	2.2*	2.0	270
(H,18,0)			
0	7.5	6.2	0
1	1.1*	4.5	90
2	2.8	3.2	0
3	2.7	1.9	90
4	3.5	3.5	180
5	8.7	6.5	90
6	1.2*	2.4	180
7	2.0*	0.7	270
8	1.9*	2.5	0
9	1.2*	1.5	270
10	2.1*	1.8	0
11	2.1*	0.7	90
12	1.3*	2.2	180
13	2.2*	1.4	90
14	2.2*	2.0	0
(H,19,0)			
1	3.6	4.0	90
2	17.3	13.4	0
3	1.8*	3.2	90
4	2.0*	0.6	0
5	8.9	7.9	270
6	5.1	3.8	180
7	2.0*	1.5	270
8	2.0*	0.9	180
9	2.1*	1.1	90
10	2.1*	0.2	180
11	2.1*	3.3	90
12	2.2*	2.2	0
13	2.2*	3.5	270
(H,20,0)			
0	8.2	8.1	0
1	1.2*	0.7	270
2	1.3*	1.4	180
3	5.5	4.4	90
4	8.3	7.5	180
5	4.8	3.6	270
6	1.3*	1.8	180
7	2.1*	2.0	90
8	1.2*	3.8	0
9	2.2*	0.5	90
10	1.4*	0.2	0
11	2.2*	3.8	270
(H,21,0)			
1	8.3	6.7	90
2	6.1	5.3	0
3	1.3*	1.6	90
4	2.1*	1.9	0
5	4.9	5.0	270
6	1.3*	2.2	180
7	1.3*	3.4	270
8	2.2*	3.2	180
9	1.3*	2.9	90
10	5.0	3.7	0
(H,22,0)			
0	6.4	5.7	0
1	1.3*	2.5	270
2	1.4*	2.0	0
3	2.2*	1.0	270
4	1.3*	0.6	180
5	4.1	4.3	90
6	1.4*	1.3	0
7	2.2*	0.4	90
8	2.2*	1.3	180
(H,23,0)			
1	1.4*	1.0	270
2	3.9	3.3	0
3	2.2*	0.6	90
4	2.2*	4.0	0
5	5.8	4.6	270
(H,0,1)			
1	35.9	39.8	90
2	87.5	82.2	90
3	26.6	29.5	90
4	10.7	11.0	270
5	56.9	58.7	270
6	21.1	23.2	270
7	17.9	17.1	90
8	5.5	3.6	90
9	36.3	38.0	90
10	14.4	13.0	90
11	3.7	3.2	90
12	5.8	5.2	90
13	4.6	2.7	90
14	7.6	6.5	270
15	0.7*	0.8	90
16	1.0*	0.3	270
17	0.9*	0.5	90
18	1.0*	1.8	90
19	1.0*	1.9	90
20	1.1*	1.2	90
21	1.1*	0.9	270
(H,1,1)			
0	11.0	12.6	270
1	49.2	47.2	118
2	64.6	60.1	119
3	38.0	36.0	77
4	68.5	67.6	206
5	17.2	18.2	294
6	21.8	27.7	345
7	6.4	6.2	214
8	13.8	14.1	50
9	12.0	12.3	291
10	23.8	25.0	164
11	10.6	9.7	265
12	6.8	6.5	234
13	8.5	8.0	104
14	7.7	7.6	43
15	5.1	5.4	300
(H,2,1)			
0	6.4	5.0	0
1	4.5	4.3	134
2	53.7	51.4	121
3	77.9	76.6	253
4	59.6	59.9	150
5	34.3	36.2	284
6	20.1	22.2	273
7	21.9	25.1	72
8	18.0	19.4	273
9	18.5	21.0	97
10	10.1	10.2	119
11	14.3	14.4	270
12	8.8	8.2	92
13	15.0	16.2	263
14	7.6	7.7	173
15	4.2	4.3	83
(H,3,1)			
0	15.8	18.9	270
1	20.6	22.3	295
2	62.6	62.8	195
3	29.4	33.6	232
4	44.7	46.6	58
5	26.6	27.0	145
6	5.6	5.2	189
7	26.3	26.0	72
8	8.2	8.7	327
9	2.2	1.9	305
10	8.8	10.1	307
11	4.3	3.7	279
12	8.7	9.6	135
13	7.6	6.5	123
14	5.8	6.8	331
(H,4,1)			
0	41.9	46.2	0
1	49.4	49.0	76
2	34.4	34.4	102
3	65.8	65.1	296
4	15.5	15.1	101
5	27.9	29.0	255
6	32.5	33.5	307
7	5.9	5.6	127
8	9.2	9.2	342
9	10.0	11.0	88
10	9.8	10.2	46
11	2.5	1.9	32
12	7.5	6.8	41
13	7.7	8.5	309
14	4.3	4.1	339
(H,5,1)			
0	21.7	25.7	90
1	23.7	24.4	98
2	29.3	29.4	185
3	23.5	23.5	83
4	24.8	25.1	232
5	14.5	14.7	79
6	27.6	28.3	40
7	7.0	6.8	18
8	7.9	6.7	300
9	5.1	4.2	345
10	16.2	16.3	178
11	9.9	10.0	142
12	8.9	10.9	223
13	2.5	2.4	219
14	3.9	3.5	85
(H,6,1)			
0	7.9	8.1	180
1	58.1	56.8	86
2	29.8	31.4	134
3	23.8	24.9	270
4	16.9	17.8	198
5	22.7	23.6	270
6	8.6	7.4	168
7	33.7	36.0	95
8	10.5	10.8	311
9	19.4	20.1	60
10	9.7	8.8	355
11	5.8	4.4	262
12	9.9	8.5	123
13	7.2	6.1	239
14	4.9	5.8	158
(H,7,1)			
0	2.7	3.5	90
1	16.3	16.3	323
2	32.4	33.3	167
3	12.9	13.0	151
4	10.5	10.2	110
5	10.4	10.7	97
6	23.8	23.9	337
7	2.1	1.6	309
8	12.3	12.9	82
9	9.8	8.4	315
10	5.7	5.4	246
11	1.4*	1.2	240
12	4.9	4.3	173
13	5.2	5.1	140
14	2.4	2.0	33
(H,8,1)			
0	17.9	19.8	180
1	11.3	11.8	25
2	33.3	35.0	76
3	18.4	18.5	308
4	20.8	21.6	150
5	12.0	12.2	241
6	34.5	35.3	229
7	7.6	7.3	251
8	13.7	15.1	310
9	3.3	2.5	194
10	10.6	10.8	79
11	8.8	8.6	345
12	5.3	5.3	105
13	7.3	7.8	245
(H,9,1)			
0	6.0	7.0	270
1	15.4	15.0	271
2	22.6	24.6	182
3	8.1	8.3	87
4	14.1	14.9	346
5	14.9	15.2	101
6	28.4	29.4	38
7	9.3	9.5	291
8	7.9	8.4	323
9	8.5	8.3	117
10	15.0	15.0	208
11	5.0	5.0	92
12	4.4	4.9	203
(H,10,1)			
0	15.0	15.0	0
1	26.2	26.2	74
2	3.2	3.3	7
3	4.5	4.0	309
4	5.3	5.9	133
5	20.9	19.7	274
6	9.1	9.0	308
7	4.7	4.7	151
8	13.9	14.5	348
9	16.1	16.8	80
10	6.5	6.6	16
11	7.5	7.6	251
12	4.0	4.3	167
(H,11,1)			
0	1.9	0.1	90
1	5.2	5.1	69
2	13.5	14.3	210
3	4.8	4.4	330
4	19.5	19.5	148
5	6.7	6.7	99
6	19.5	21.1	354
7	6.0	6.2	32
8	13.6	14.0	341
9	12.1	12.4	297
10	16.2	15.6	182
11	7.4	7.5	158
(H,12,1)			
0	27.5	28.5	0
1	14.2	14.1	129
2	17.2	17.4	107
3	8.2	8.2	79
4	20.0	19.8	179
5	5.9	5.8	247
6	10.7	10.9	225
7	8.2	8.3	77
8	6.4	6.6	250
9	6.4	6.3	101
10	5.9	5.9	17
(H,13,1)			
0	9.7	11.0	270
1	13.7	13.1	31
2	7.6	8.5	159
3	10.4	10.1	177
4	8.1	8.1	17
5	10.7	10.3	252
6	15.2	15.2	18
7	3.4	3.8	351
8	2.2	2.4	150
9	3.5	3.7	334
(H,14,1)			
0	1.4	0.6	0
1	16.9	16.8	46
2	3.6	3.2	344
3	13.9	13.6	281
4	5.1	4.9	131
5	11.9	11.3	267
6	0.8	0.6	228
7	7.3	7.7	163
8	6.6	6.8	294
(H,15,1)			
0	5.0	5.1	270
1	2.1	2.8	260
2	20.3	19.5	194
3	5.5	5.4	116
4	4.4	4.1	70
5	1.1	1.7	83
6	10.9	11.4	18
(H,16,1)			
0	15.6	15.5	0
1	5.4	5.4	109
2	9.1	9.1	41
3	4.0	4.0	303
4	3.5	3.3	153
(H,0,2)			
0	96.4	96.2	180
1	6.1	6.0	0
2	23.2	22.9	180
3	4.0	0.8	180
4	18.5	22.6	0
5	15.2	17.8	0
6	25.1	27.5	180
7	2.3	1.7	180
8	5.2	3.0	0
9	3.1	4.0	180
10	9.4	8.6	180
11	3.7	4.0	0
12	4.2	2.9	0
13	7.6	7.7	180
14	3.8	1.9	180
15	6.1	4.8	0
16	5.4	4.9	180
17	1.2*	2.1	0
18	1.3*	2.2	180
19	6.0	5.0	180
20	6.3	4.9	0
21	1.4*	0.3	0
(H,1,2)			
0	30.4	32.5	90
1	37.6	37.6	239
2	30.0	29.3	56
3	6.5	7.5	281
4	22.3	23.1	232
5	27.4	28.2	93
6	7.1	6.3	273
7	11.5	11.2	21
8	22.5	23.0	51
9	10.4	9.8	176
10	4.5	4.6	99
11	10.1	10.0	225
12	12.0	11.2	332
13	6.0	5.8	283
14	3.1	4.1	264
(H,2,2)			
0	30.2	30.9	180
1	55.2	55.2	200
2	19.8	22.9	318
3	46.5	47.0	172
4	25.0	26.2	44
5	31.6	32.3	327
6	21.4	23.3	287
7	35.7	38.8	348
8	15.3	17.2	180
9	6.2	6.2	149
10	14.2	15.7	35
11	17.2	18.1	216
12	11.3	11.3	321
13	6.5	6.8	336
14	6.4	6.4	327
(H,3,2)			
0	48.8	52.5	90
1	8.8	8.7	216
2	24.9	23.8	338
3	38.0	38.3	322
4	25.0	24.0	276
5	5.6	4.7	58
6	12.7	13.7	291
7	38.4	39.0	114
8	4.3	2.7	2
9	1.0*	0.5	233
10	13.9	15.7	117
11	9.7	10.6	334
12	6.8	5.9	225
13	4.0	3.6	80
14	6.8	10.1	287
(H,4,2)			
0	5.3	5.3	180
1	39.8	41.8	122
2	51.2	51.5	116
3	21.9	22.6	119
4	33.3	33.7	334
5	11.0	12.3	332
6	10.2	11.1	310
7	13.4	13.8	2
8	12.1	11.1	228
9	8.8	8.3	100
10	3.3	3.3	194
11	10.4	12.2	155
12	13.3	15.2	38
13	5.1	4.4	353

Table 4 (*cont.*)

H	OBS	CALC	ALPHA
(H,4,2)			
14	3.7	3.7	186
(H,5,2)			
0	1.6	0.1	270
1	23.5	24.1	346
2	14.0	13.9	60
3	11.4	11.8	241
4	5.0	2.3	46
5	10.9	10.6	58
6	6.2	5.9	270
7	6.1	5.4	83
8	8.7	8.9	83
9	11.1	11.0	336
10	6.6	7.2	57
11	11.4	12.6	261
12	4.0	3.6	242
13	4.4	4.8	179
14	3.5	5.0	194
(H,6,2)			
0	22.4	22.9	180
1	23.1	22.6	167
2	7.0	6.3	275
3	30.5	30.7	189
4	9.8	9.4	194
5	22.1	21.9	353
6	3.8	3.8	217
7	13.6	13.1	5
8	22.2	22.6	193
9	13.9	14.2	186
10	1.5*	0.3	109
11	8.1	7.7	230
12	6.4	6.5	340
13	2.9	3.0	283
(H,7,2)			
0	16.8	18.5	90
1	20.2	20.3	245
2	16.0	15.8	46
3	25.7	26.6	289
4	27.8	28.9	293
5	4.7	4.0	287
6	14.0	13.2	296
7	22.8	22.6	95
8	19.3	18.4	83
9	8.1	8.0	189
10	7.0	6.8	80
11	5.2	5.3	281
12	5.1	3.9	291
13	0.7*	1.0	37
(H,8,2)			
0	4.1	3.4	0
1	18.6	20.0	92
2	9.5	9.1	83
3	20.1	19.9	232
4	25.4	27.3	21
5	10.3	10.6	230
6	17.5	18.8	285
7	15.0	15.2	338
8	7.2	7.7	217
9	4.9	5.0	297
10	2.5	2.8	109
11	8.5	9.2	150
12	8.6	9.4	10
(H,9,2)			
0	30.7	32.1	90
1	15.5	15.8	335
2	13.3	13.6	234
3	15.5	15.5	270
4	28.0	28.9	293
5	17.1	17.3	134
6	6.1	5.8	210
7	6.0	6.4	65
8	6.5	7.0	104
9	9.0	8.7	334
10	7.5	8.0	42
11	6.5	6.7	291
12	8.1	7.9	233
(H,10,2)			
0	12.9	12.5	180
1	19.6	19.4	145
2	28.4	29.0	65
3	3.1	3.0	170
4	6.6	6.5	322
5	9.1	8.9	34
6	11.2	11.4	217
7	8.4	8.5	110
8	6.4	6.2	212
9	6.4	6.6	122
10	3.4	3.2	0
11	4.9	5.3	159
(H,11,2)			
0	9.7	9.5	90
1	29.6	29.4	256
2	5.9	6.3	357
3	17.9	17.3	296
4	10.3	11.0	242
5	12.4	12.4	14
6	0.7*	1.4	291
7	9.3	9.7	170
8	10.8	10.8	82
9	0.3*	0.9	251
10	2.7	3.3	92
(H,12,2)			
0	7.3	6.7	180
1	4.3	4.3	175
2	5.9	6.0	85
3	11.1	11.0	172
4	8.1	8.7	19
5	14.0	14.3	278
6	10.8	10.7	219
7	6.0	6.2	322
8	7.7	7.8	212
9	5.1	5.4	126
(H,13,2)			
0	10.8	10.6	90
1	5.8	5.3	323
2	7.7	7.5	32
3	14.2	14.0	245
4	17.1	16.9	255
5	11.6	11.6	151
6	6.5	7.0	275
7	7.1	6.8	82
8	9.0	8.9	62

H	OBS	CALC	ALPHA
(H,14,2)			
0	2.4	1.5	0
1	3.2	3.4	180
2	9.6	10.2	61
3	9.3	9.0	200
4	11.0	11.0	58
5	4.2	4.9	328
6	9.3	9.1	314
7	9.0	8.8	4
(H,15,2)			
0	6.5	6.4	90
1	7.8	7.8	280
2	7.5	7.2	222
3	7.8	7.5	281
4	7.0	6.6	241
5	6.2	6.7	192
(H,16,2)			
0	1.3	1.2	0
1	3.0	4.3	138
2	3.2	4.1	101
(H,0,3)			
1	7.1	6.6	270
2	46.1	47.3	270
3	14.4	15.7	270
4	5.1	2.3	90
5	9.3	8.9	90
6	19.5	19.2	90
7	11.6	10.1	270
8	5.9	0.9	90
9	20.9	20.1	270
10	27.7	26.1	270
11	11.4	10.5	90
12	4.5	2.6	270
13	3.7	2.7	270
14	10.9	10.0	90
15	12.5	11.5	270
16	1.2*	0.3	90
17	1.3*	4.5	90
18	4.7	3.9	270
19	1.4*	1.7	90
20	1.4*	1.4	270
(H,1,3)			
0	11.1	10.6	270
1	11.2	12.1	204
2	16.6	17.6	244
3	10.7	11.8	47
4	5.6	5.1	325
5	15.7	14.9	346
6	14.1	14.0	63
7	7.0	7.2	295
8	18.8	19.8	286
9	19.7	19.7	150
10	6.6	5.7	42
11	5.0	5.8	128
12	6.1	5.1	219
13	6.5	5.3	25
(H,2,3)			
0	2.7	1.5	0
1	12.6	13.6	166
2	37.3	39.7	313
3	15.2	16.7	78
4	11.0	12.1	272
5	9.0	9.2	79
6	24.7	25.0	133
7	8.2	7.6	207
8	17.9	17.8	9
9	8.4	7.9	319
10	7.9	7.7	293
11	2.7	2.3	226
12	6.6	6.6	223
13	7.7	7.0	85
(H,3,3)			
0	20.0	20.4	90
1	23.0	23.3	238
2	16.3	18.4	330
3	21.9	22.3	342
4	8.9	9.4	320
5	34.1	35.2	22
6	13.9	14.1	220
7	6.4	5.9	215
8	10.1	11.0	109
9	8.9	9.5	226
10	2.6	1.7	328
11	3.1	2.9	216
12	4.1	4.2	150
13	6.4	7.6	3
(H,4,3)			
0	6.8	6.5	180
1	9.4	10.3	245
2	30.6	31.7	241
3	19.0	20.3	137
4	4.5	4.4	256
5	7.5	7.1	100
6	25.7	25.8	77
7	8.1	7.5	323
8	11.1	11.1	188
9	8.8	9.4	159
10	15.2	15.6	243
11	2.1	1.9	231
12	3.4	3.2	206
13	3.9	4.2	207
(H,5,3)			
0	31.3	33.7	270
1	23.1	22.0	173
2	15.8	15.0	80
3	11.9	12.0	318
4	18.0	17.8	169
5	17.0	18.1	326
6	4.5	2.6	38
7	7.0	6.7	217
8	15.4	17.5	352
9	14.5	15.4	168
10	7.0	6.4	47
11	5.1	4.5	71
12	4.6	4.8	129
13	3.3	5.6	305
(H,6,3)			
0	19.8	16.9	0
1	9.5	8.5	206
2	21.5	22.6	304
3	16.8	18.1	193
4	4.5	5.2	123

H	OBS	CALC	ALPHA
(H,6,3)			
5	11.4	10.5	304
6	12.2	11.0	155
7	5.9	5.0	310
8	5.5	3.1	121
9	5.9	6.1	250
10	7.7	6.9	306
11	5.4	4.8	179
12	5.1	5.1	303
(H,7,3)			
0	4.9	5.0	90
1	22.5	22.7	159
2	23.2	24.0	311
3	17.7	16.6	25
4	3.1	2.8	190
5	11.4	10.9	333
6	8.0	7.7	254
7	4.9	3.1	209
8	5.5	4.8	252
9	11.2	10.7	182
10	2.6	3.0	150
11	2.0	1.3	167
12	2.1	2.6	49
(H,8,3)			
0	2.6	0.6	0
1	22.9	23.5	226
2	24.9	24.3	271
3	22.9	24.1	98
4	5.3	5.3	18
5	13.3	13.2	91
6	21.5	22.4	68
7	7.8	7.6	347
8	5.7	4.9	89
9	2.9	2.1	158
10	10.8	11.2	250
11	6.7	6.7	180
(H,9,3)			
0	10.0	9.8	270
1	12.7	13.0	176
2	16.2	16.1	157
3	9.8	9.3	318
4	3.6	2.4	138
5	20.1	19.7	337
6	5.9	5.8	229
7	5.1	4.5	107
8	2.8	2.5	294
9	5.3	5.0	166
10	9.2	9.4	55
11	2.9	3.3	275
(H,10,3)			
0	13.8	13.7	0
1	2.8	2.2	117
2	4.0	6.4	182
3	19.4	19.1	214
4	10.9	11.0	203
5	7.4	7.5	70
6	11.6	11.8	90
7	5.9	6.4	347
8	8.3	8.2	172
9	4.6	4.1	276
10	4.8	4.6	257
(H,11,3)			
0	5.9	6.3	90
1	14.2	14.0	188
2	2.7	2.6	103
3	2.5	0.6	350
4	4.4	4.5	304
5	11.4	11.1	21
6	4.1	4.6	239
7	8.9	8.5	202
8	8.4	7.8	87
9	13.0	12.2	202
(H,12,3)			
0	2.4	0.7	180
1	10.1	10.2	236
2	12.5	12.2	299
3	2.3	1.4	188
4	3.2	2.8	80
5	5.5	5.0	66
6	7.4	7.4	120
7	6.1	6.4	343
8	11.3	11.7	22
(H,13,3)			
0	1.8	1.6	90
1	17.3	16.9	180
2	5.4	5.3	351
3	13.7	12.8	13
4	5.9	6.1	214
5	8.2	7.9	13
6	5.9	6.1	182
(H,14,3)			
0	4.5	3.7	180
1	7.9	7.9	207
2	1.4	2.1	315
3	12.0	11.6	145
4	2.3	2.4	45
(H,15,3)			
1	5.9	6.9	204
(H,0,4)			
0	6.5	6.4	180
1	20.8	19.7	0
2	5.2	4.2	0
3	20.6	20.2	0
4	23.3	22.8	0
5	18.8	18.2	180
6	1.7*	2.5	180
7	17.4	15.3	180
8	8.3	7.6	180
9	6.0	5.9	0
10	5.9	6.3	180
11	10.9	8.9	0
12	14.7	12.8	0
13	1.1*	2.2	0
14	1.2*	0.0	90
15	3.3	4.4	180
16	1.3*	0.6	0
17	1.3*	0.5	0
18	1.4*	1.4	180
19	1.3*	1.9	0

H	OBS	CALC	ALPHA
(H,1,4)			
0	20.2	21.2	270
1	6.6	6.5	22
2	13.8	14.0	206
3	8.7	7.5	241
4	14.7	15.8	30
5	18.0	18.8	321
6	9.3	8.6	205
7	11.3	9.8	84
8	6.6	5.8	253
9	11.3	9.9	120
10	3.7	3.1	335
11	7.0	6.8	324
12	8.2	8.1	171
(H,2,4)			
0	1.3*	1.0	0
1	21.0	22.0	32
2	1.3*	2.8	176
3	19.2	19.1	341
4	13.4	13.2	205
5	16.0	16.3	145
6	9.8	10.6	47
7	17.8	18.3	193
8	6.7	6.4	144
9	1.6*	2.8	50
10	1.0*	0.7	73
11	9.9	9.8	48
12	5.3	5.6	175
(H,3,4)			
0	1.2*	1.6	90
1	1.4*	3.4	238
2	15.1	15.1	170
3	6.7	6.5	220
4	6.1	6.0	87
5	2.0*	4.3	141
6	8.8	8.9	56
7	4.7	3.8	311
8	6.2	6.5	260
9	3.6	3.8	311
10	1.1*	2.0	57
11	0.9*	1.6	133
(H,4,4)			
0	1.8*	3.4	0
1	16.6	17.9	324
2	5.3	5.1	162
3	11.9	13.1	339
4	10.6	10.3	32
5	10.5	9.8	175
6	9.1	8.9	186
7	14.9	15.1	153
8	1.6*	2.8	148
9	7.3	6.8	294
10	1.2*	3.6	232
11	6.6	8.4	346
(H,5,4)			
0	24.9	24.3	270
1	11.0	11.3	228
2	14.6	15.1	344
3	16.2	16.7	262
4	13.3	13.5	123
5	6.4	7.2	168
6	1.8*	1.7	201
7	10.5	10.7	91
8	7.9	8.0	282
9	6.5	7.1	108
10	5.3	5.6	279
11	3.4	4.5	239
(H,6,4)			
0	11.5	12.8	180
1	17.4	17.2	49
2	16.0	16.1	322
3	20.5	20.3	352
4	2.2*	1.8	228
5	14.4	12.3	247
6	11.0	10.5	60
7	15.3	14.6	167
8	10.6	10.2	36
9	9.0	8.6	72
10	1.3*	1.9	202
(H,7,4)			
0	1.7*	0.8	270
1	8.2	8.4	284
2	12.6	12.1	189
3	9.4	9.5	119
4	8.4	7.1	107
5	9.5	8.5	5
6	1.9*	2.9	198
7	7.4	5.5	328
8	9.8	9.8	287
9	1.4*	0.7	73
10	1.1*	2.8	4
(H,8,4)			
0	0.4*	0.8	180
1	7.2	7.8	356
2	5.6	6.5	207
3	8.2	8.7	355
4	5.1	5.3	37
5	5.8	6.2	163
6	8.6	9.6	131
7	6.6	7.8	153
8	4.5	4.2	204
9	8.1	8.9	58
(H,9,4)			
0	8.4	8.1	270
1	5.8	6.1	129
2	10.2	10.9	19
3	8.0	8.7	276
4	13.8	13.4	111
5	5.0	5.0	204
6	7.7	7.6	113
7	2.1	2.3	139
8	7.3	7.3	308
9	4.1	4.8	68
(H,10,4)			
0	3.6	3.5	0
1	14.6	14.7	5
2	7.5	8.0	244
3	12.7	12.9	350
4	1.1	1.4	240
5	9.3	8.9	235
6	10.6	11.1	8
7	8.0	7.7	200
8	4.8	5.5	148

H	OBS	CALC	ALPHA
(H,11,4)			
0	14.0	13.6	270
1	4.5	5.4	148
2	8.8	9.5	164
3	0.4*	0.3	71
4	9.3	9.4	111
5	2.7	3.0	300
6	11.1	11.3	326
7	10.5	11.8	85
(H,12,4)			
0	1.2	0.6	0
1	6.0	5.4	43
2	2.0	2.8	287
3	7.0	7.0	353
4	1.5	2.1	312
5	2.9	2.8	217
(H,13,4)			
0	3.7	3.4	270
1	5.3	5.3	292
2	4.9	5.2	193
3	2.7	2.7	259
(H,0,5)			
1	5.2	1.5	270
2	5.4	1.8	90
3	7.7	6.6	90
4	16.1	16.0	90
5	9.2	7.3	90
6	10.0	8.6	270
7	1.5*	2.4	270
8	7.0	7.0	270
9	3.9	2.2	90
10	13.9	12.6	90
11	2.8	3.2	270
12	4.2	3.2	90
13	3.4	3.2	90
14	2.8	2.5	270
15	6.2	4.8	90
16	1.3*	0.5	90
17	1.3*	2.8	270
18	1.4*	1.9	270
(H,1,5)			
0	1.4*	1.3	270
1	10.7	10.5	51
2	10.2	9.4	58
3	5.4	4.8	207
4	2.8	1.5	62
5	8.0	6.9	180
6	9.9	8.3	126
7	8.2	7.6	32
8	4.0	3.3	263
9	11.5	10.1	314
10	3.2	3.0	92
(H,2,5)			
0	1.4*	2.7	0
1	20.6	20.3	303
2	18.3	18.0	120
3	11.4	9.9	58
4	4.5	4.5	307
5	13.8	13.0	118
6	7.4	7.0	321
7	1.1*	0.2	120
8	7.5	7.3	167
9	7.8	7.7	266
(H,3,5)			
0	8.6	8.6	90
1	7.6	8.0	138
2	4.2	3.9	285
3	7.1	7.3	186
4	1.4*	1.9	202
5	5.8	6.0	266
6	4.8	4.1	308
7	1.1*	1.4	73
8	7.0	7.4	116
9	3.3	4.0	99
(H,4,5)			
0	1.7*	2.8	180
1	8.0	8.3	214
2	14.4	14.9	67
3	2.2*	4.1	93
4	2.1*	3.8	343
5	5.7	4.5	55
6	9.8	9.3	273
7	1.3*	1.2	5
8	1.1*	1.1	5
9	6.6	9.0	311
(H,5,5)			
0	6.1	6.5	270
1	11.6	12.2	331
2	5.0	5.5	81
3	4.9	4.1	142
4	6.2	6.6	331
5	6.2	6.4	151
6	4.5	5.0	230
7	3.6	4.0	70
8	5.2	7.1	226
9	3.2	4.0	356
(H,6,5)			
0	7.0	8.1	180
1	10.3	10.5	318
2	11.8	11.5	99
3	1.9*	4.2	37
4	7.8	7.7	72
5	14.9	16.1	83
6	11.7	11.7	285
(H,7,5)			
0	5.8	5.9	90
1	1.7*	2.1	22
2	1.8*	2.3	229
3	5.8	5.3	226
4	8.5	8.5	65
5	1.5*	1.2	295
6	7.9	8.6	138
7	5.8	5.9	11
(H,8,5)			
0	1.0	1.8	180
1	5.4	5.5	211
2	5.0	4.9	103

H	OBS	CALC	ALPHA
(H,8,5)			
3	2.3	2.4	258
4	8.1	8.6	306
5	1.9	1.5	122
6	1.5	3.2	212
7	2.3	2.4	346
(H,9,5)			
0	2.6	2.5	90
1	6.5	6.7	330
2	9.9	10.4	12
3	6.9	6.9	205
4	5.8	5.6	262
5	8.8	9.5	155
6	0.1*	0.6	228
(H,10,5)			
0	9.1	9.7	180
1	6.0	6.1	276
2	6.5	7.0	71
3	7.9	8.6	72
4	5.5	6.7	33
(H,11,5)			
0	1.2	0.6	270
1	5.2	6.3	354
(H,0,6)			
0	4.9	2.3	0
1	11.7	10.1	180
2	4.5	3.2	180
3	3.2	1.2	180
4	3.6	0.9	0
5	10.2	8.7	0
6	7.3	6.3	180
7	1.1*	0.3	180
8	12.1	9.7	0
9	5.3	3.8	180
10	1.2*	0.7	0
11	6.4	4.9	180
12	7.2	6.0	180
13	3.2	2.0	0
14	1.3*	1.0	180
15	1.4*	1.8	0
16	1.4*	1.7	0
(H,1,6)			
0	11.6	10.0	90
1	6.8	5.6	144
2	5.7	5.1	190
3	3.8	2.7	84
4	5.0	4.6	204
5	3.2	2.7	186
6	5.7	5.3	40
(H,2,6)			
0	11.4	9.9	0
1	4.5	4.4	287
2	6.7	6.3	354
3	5.5	5.6	96
4	12.9	11.5	182
5	5.3	4.9	281
6	2.3	2.1	95
(H,3,6)			
0	5.9	7.3	270
1	4.1	4.2	352
2	5.2	5.7	17
3	7.0	7.2	108
4	4.5	4.4	283
(H,4,6)			
0	8.9	9.5	0
1	1.5*	2.2	339
2	6.0	6.3	245
3	1.1*	0.5	66
4	4.4	4.7	178
5	4.6	6.0	61
(H,5,6)			
0	11.2	14.1	90
1	5.0	6.1	111
2	1.1*	1.6	150
3	4.6	5.0	8
4	4.7	5.7	264
(H,0,7)			
1	1.1*	0.5	90
2	10.1	7.6	90
3	5.5	3.4	270
4	1.2*	2.7	270
5	1.1*	1.3	270
6	1.2*	0.2	270
7	5.9	4.5	90
8	1.2*	3.0	270
9	1.2*	1.8	90
10	1.3*	2.5	270
11	6.0	3.6	270
12	1.4*	2.2	90
13	1.3*	1.8	270
14	1.4*	1.1	270
(H,0,8)			
0	6.3	4.8	0
1	1.3*	2.4	0
2	1.3*	2.9	180
3	5.9	4.8	180
4	1.3*	0.8	0
5	1.3*	2.0	180
6	1.3*	0.6	180
7	7.3	5.4	0
8	1.3*	1.5	180
9	1.4*	0.0	90
10	1.4*	0.6	180
11	1.4*	0.1	180
(H,0,9)			
1	1.4*	1.7	270
2	1.4*	2.1	270
3	1.4*	2.5	90
4	1.4*	1.1	270
5	1.4*	0.6	270

values of $(|F_o| - |F_c|)$ were omitted from the calculation. The quantity minimized was $\Sigma w(|kF_o| - |F_c|)^2$. In the final stages of the refinement only the observed data were used.

The hydrogen atoms were located from a difference map as shown in Fig. 2. One of the oxygen atoms, O(3), may well be disordered in the crystal and therefore the location of the hydrogen atom, H(7), attached to it is uncertain. For this reason parameters for H(7) were not included in the final structure factor calculation for Cu–Mo data. The area of H(7) appears as a blur in the final difference map and the parameters of the maximum are listed in Table 3. The parameters from the Cr data have been used in computing distances and angles.

When the R value for the observed data only was 7·4 % a secondary extinction correction was applied in the form

$$F_{\text{corr}} = F_{\text{obs}}(1 + \alpha\beta_{(2\theta)} \text{ Lp } |F_{\text{obs}}|^2)$$

(Zachariasen, 1963*a*). Values of $\beta_{(2\theta)}$ for $\mu r = 0{\cdot}77$ were given by Zachariasen (1963*b*) and α was found to be $1{\cdot}4 \times 10^{-5}$ (maximum correction 23 %). The R value was reduced to 6·5 % for the observed data and 8·3 % for all the data. The final parameters are listed in Tables 2 and 3. The standard errors listed are obtained from the inverted block diagonal least squares matrices. A list of observed and calculated structure factors is given in Table 4.

(*b*) Cr *data*

The Cr data were refined at Oak Ridge National Laboratory with a full-matrix least-squares program which calculates structure factors and derivatives using complex scattering factors. The value of $\Delta f''$ was considered to be independent of $\sin\theta/\lambda$ and was included as a variable in the refinement. Results for this parameter are listed in Table 5. An extinction correction was applied for $\mu r = 2{\cdot}0$, and the value of α was found to be 3×10^{-5} (maximum correction 11 %). (A correction for anomalous dispersion was applied to the Cu–Mo data in a different manner. Therefore the respective values of α obtained should not be compared.) The initial positional and temperature parameters used were those found for the Cu–Mo data. Reflections were omitted from the least-squares calculation if $(|F_o| - |F_c|)$ was greater than either 3·0 or $10\sigma|F_o|$. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, with weights based on the experimental uncertainties (Johnson, 1965). The hydrogen atoms were given the anisotropic temperature factors of the atoms to which they were attached but these values were not refined. The final R value for all the observed data is 2·3 %. The refined parameters together with their standard deviations are listed in Tables 2 and 3 together with those derived from the Cu–Mo data. The standard errors were obtained from the inverted full matrices. The maximum value of

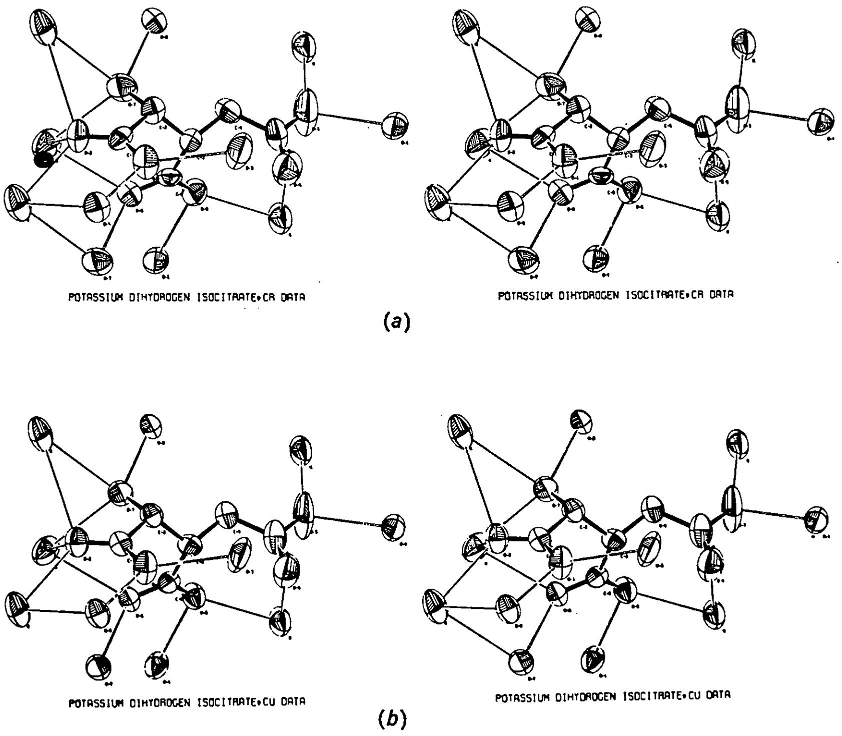


Fig. 3. Stereodiagrams representing the principal axes of the thermal ellipsoids. (*a*) Cr data, (*b*)Cu–Mo data.

$\sin\theta/\lambda$ is less for the Cr data (0·43 Å^{-1}) than for the Cu data (0·64 Å^{-1}) which may in part account for the discrepancy in R factors. A list of calculated and observed structure factors is given in Table 6.

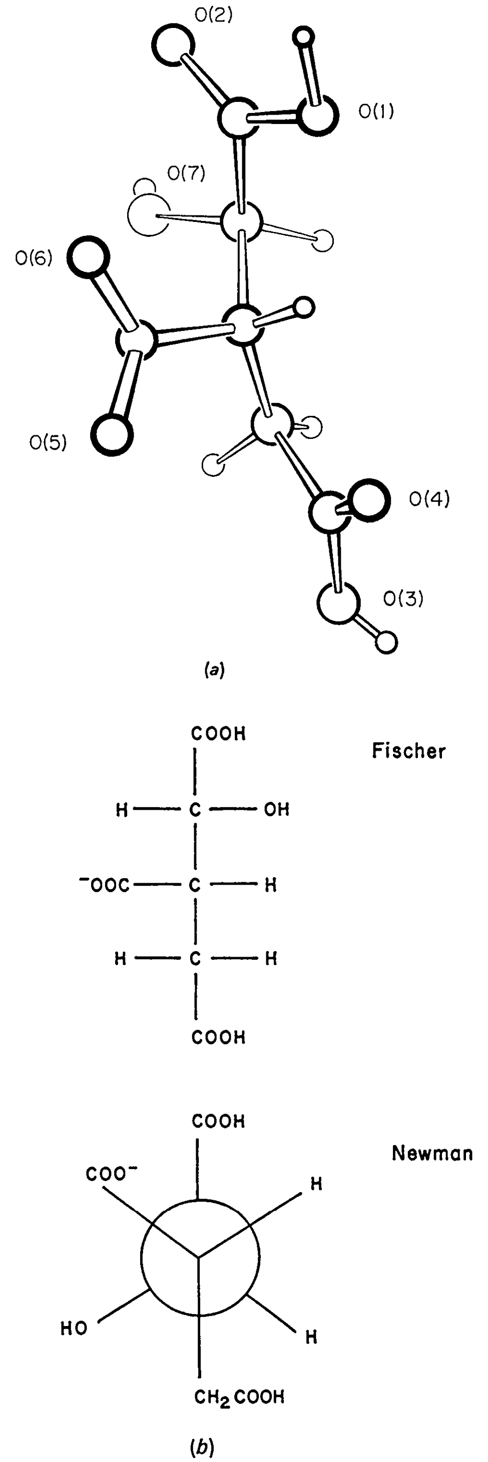


Fig. 4. The absolute configuration and shape of the isocitrate ion. (*a*) View along the plane through C(1), C(2) and C(3). (*b*) Representations of the absolute configuration determined.

Table 5. *Values of* $\Delta f''$ *determined from the* Cr *data*

	$\Delta f''$	$\sigma\Delta f''$	$\overline{\Delta f''}$	*International Tables* value
K	2·38	0·08	2·38	2·2–2·1
O(1)	0·16	0·05	0·19	0·2–0·1
O(2)	0·14	0·05		
O(3)	0·14	0·06		
O(4)	0·27	0·06		
O(5)	0·23	0·05		
O(6)	0·24	0·05		
O(7)	0·15	0·05		
C(1)	0·08	0·04	0·07	0·1
C(2)	0·02	0·05		
C(3)	0·06	0·05		
C(4)	0·09	0·04		
C(5)	0·06	0·05		
C(6)	0·11	0·04		

The principal axes of the thermal ellipsoids were determined and the magnitudes and their direction cosines with respect to the cell axes are listed in Table 7 for the two sets of data. They are illustrated in stereodiagrams in Fig. 3. The standard deviations in temperature factors are 0·08 Å^2 for the potassium ion and 0·3 Å^2 for carbon and oxygen atoms. This information and a comparison of the results in Table 7 indicate that all carbon atoms and also O(5) and O(6) are not significantly anisotropic.

Computations

The reduction of the data and the computations of the $|F|^2$, P_c and P_s maps were carried out on an IBM 1620 computer using programs written in this laboratory. The block-diagonal least-squares refinement of the Cu–Mo data was also performed on the IBM 1620 computer. For a complete list of programs used with the IBM 1620 see Johnson (1965).

The full-matrix least-squares refinement of the Cr data was done on a CDC 1604 computer using a modification of the *ORFLS* program by Dr W. R. Busing, Mrs K. O. Martin and Dr H. A. Levy. Fig. 3 was plotted with the program *ORTEP* written by C.K.J. We are indebted to The Oak Ridge National Laboratory for these uses of the 1604 computer.

The atomic scattering factors used were from *International Tables for X-ray Crystallography* (1962*a*), for carbon, oxygen and potassium. For the ionized oxygen atoms of the carboxyl groups the average of the scattering factors for oxygen as O and O$^-$ were used. For the Cu–Mo data the scattering factors for hydrogen atoms used were those of Stewart, Davidson & Simpson (1965).

Discussion of the structure

The absolute configuration of the isomer of isocitric acid which is active in the tricarboxylic acid cycle has been determined from the anomalous dispersion data (*via* the P_s map from the Cr data). The result is shown in Fig. 4 and agrees with the result for the lactone (Patterson *et al.*, 1962). (For references to chemical studies on the absolute configuration of naturally occurring isocitric acid see Glusker, Van der Helm, Love, Dornberg, Minkin, Johnson & Patterson, 1963.) The correct configurational formula for (+)-isocitric acid is (1*R*:2*S*)-1-hydroxy-1,2,3-propanetricarboxylic acid (Cahn, Ingold & Prelog, 1966).

The bond distances and angles in the isocitrate ion which are derived from the weighted averages of par-

Table 6. *Observed and calculated structure factors* (Cr *data*)

The observed data are corrected for extinction. Measurements listed for reflections *hkl* are an average of those for *hkl* and $\bar{h}k\bar{l}$ and measurements listed for $\bar{h}kl$ are the average of $\bar{h}kl$ and $hk\bar{l}$. For each reflection the observed and calculated structure factors are given (in electrons) followed by the phase angle (°). Reflections which were too weak for measurements are not included in this table.

H	K	L	OBS	CALC	ALPHA
0	0	2	92.8	94.1	184
0	0	4	7.6	7.5	193
0	1	1	12.9	11.9	267
0	1	2	30.5	31.5	100
0	1	3	12.6	11.9	272
0	1	4	20.6	20.5	282
0	2	0	14.0	12.0	136
0	2	1	3.5	3.3	7
0	2	2	30.6	31.3	188
0	2	4	2.2	2.5	342
0	3	1	17.5	18.7	273
0	3	2	49.5	52.0	96
0	3	3	21.5	20.3	93
0	3	4	4.5	4.4	44
0	4	0	98.5	97.7	5
0	4	1	42.4	41.9	2
0	4	2	11.3	6.3	227
0	4	3	4.9	5.0	185
0	4	4	3.4	3.5	344
0	5	1	24.5	25.0	90
0	5	2	4.3	4.3	183
0	5	3	31.8	31.6	270
0	6	0	63.4	63.9	8
0	6	1	8.7	8.8	172
0	6	2	22.1	21.2	192
0	6	3	19.0	18.2	4
0	7	1	4.0	4.1	83
0	7	2	18.0	18.4	105
0	7	3	3.2	3.4	100
0	8	0	24.1	24.6	14
0	8	1	18.2	18.4	177
0	8	2	4.2	4.5	314
0	8	3	.7	1.0	161
0	9	1	6.0	5.7	281
0	9	2	31.0	31.6	98
0	10	0	27.8	28.6	12
0	10	1	14.3	13.8	9
0	10	2	12.4	12.4	194
1	0	1	36.6	37.7	100
1	0	2	7.4	7.1	332
1	0	3	6.1	6.2	280
1	0	4	19.6	19.4	10
1	1	0	32.0	31.2	101
1	1	1	48.6	50.4	116
-1	1	1	43.5	45.6	243
1	1	2	35.5	36.1	244
-1	1	2	38.7	38.3	125
1	1	3	14.2	14.3	216
-1	1	3	11.5	11.5	178
1	1	4	6.8	6.9	16
-1	1	4	5.7	6.0	346
1	2	0	22.4	24.3	89
1	2	1	8.7	8.8	152
-1	2	1	4.4	4.3	124
1	2	2	57.4	56.1	203
-1	2	2	54.9	53.8	347
1	2	3	12.4	12.6	167
-1	2	3	13.9	14.0	18
1	2	4	22.1	22.0	38
-1	2	4	20.1	20.4	160
1	3	0	25.3	26.7	260
1	3	1	19.0	19.2	299
-1	3	1	22.9	23.7	68
1	3	2	6.4	6.6	216
-1	3	2	11.7	11.7	156
1	3	3	26.3	25.7	244
-1	3	3	20.7	20.0	128
1	4	0	47.7	47.0	272
1	4	1	48.4	48.6	83
-1	4	1	49.8	49.9	110
1	4	2	37.8	39.2	125
-1	4	2	43.5	44.4	64
1	4	3	10.0	10.3	254
-1	4	3	9.5	9.8	298
1	4	4	15.9	16.1	331
-1	4	4	19.3	19.3	226
1	5	0	29.4	28.9	101
1	5	1	26.2	25.1	100
-1	5	1	21.5	20.8	263
1	5	2	25.5	25.4	349
-1	5	2	21.0	21.2	20
1	5	3	23.0	22.7	185
-1	5	3	23.1	22.9	196
1	6	0	36.2	35.7	274
1	6	1	58.3	57.4	93
-1	6	1	57.9	57.1	99
1	6	2	23.2	22.0	178
-1	6	2	23.5	22.9	20
1	6	3	8.0	8.3	214
-1	6	3	9.1	9.0	344
1	7	0	12.1	12.8	111
1	7	1	15.0	14.6	328
-1	7	1	17.7	17.9	46
1	7	2	18.2	19.1	250
-1	7	2	22.2	22.0	123
1	7	3	21.1	21.5	167
-1	7	3	22.7	23.3	212
1	8	0	29.1	28.6	274
1	8	1	8.5	8.6	46
-1	8	1	14.2	13.8	164
1	8	2	15.0	14.7	95
-1	8	2	20.5	20.2	92
1	8	3	22.2	21.6	235
-1	8	3	21.9	21.2	316
1	9	0	13.7	13.3	107
1	9	1	13.6	13.9	273
-1	9	1	17.1	17.1	88
1	9	2	17.0	16.9	342
-1	9	2	14.2	14.4	38
1	10	0	16.1	17.7	278
1	10	1	25.1	24.5	83
-1	10	1	25.8	25.4	117
1	10	2	18.7	18.6	154
-1	10	2	20.1	19.0	43
1	11	0	25.7	26.0	100
2	0	0	2.7	4.5	159
2	0	1	80.1	81.6	93
2	0	2	23.2	25.4	182
2	0	3	44.6	46.2	278
2	0	4	6.8	5.9	1
2	1	0	17.9	19.2	2
2	1	1	53.5	55.4	122
-2	1	1	65.3	67.0	64
2	1	2	29.6	29.2	57
-2	1	2	30.3	29.8	128
2	1	3	15.9	16.4	248
-2	1	3	17.7	18.5	295
2	1	4	12.6	12.7	212
-2	1	4	13.3	13.3	336
2	2	0	37.2	37.1	1
2	2	1	53.7	55.6	128
-2	2	1	49.6	51.7	240
2	2	2	22.7	22.7	319
-2	2	2	22.9	22.9	40
2	2	3	41.6	42.9	322
-2	2	3	34.6	35.5	52
2	2	4	2.7	2.8	200
-2	2	4	3.3	3.3	187
2	3	0	15.5	13.8	180
2	3	1	62.8	63.7	202
-2	3	1	59.1	60.1	350
2	3	2	24.7	24.4	338
-2	3	2	25.4	25.5	203
2	3	3	16.5	16.3	336
-2	3	3	17.7	18.4	214
2	3	4	15.2	15.6	172
-2	3	4	16.0	15.8	15
2	4	0	25.4	25.6	3
2	4	1	36.1	35.8	108
-2	4	1	34.3	33.4	264
2	4	2	51.5	49.8	117
-2	4	2	51.4	48.7	248
2	4	3	28.0	28.5	251
-2	4	3	32.5	32.9	129
2	4	4	4.2	4.3	152
-2	4	4	5.1	5.2	211
2	5	0	56.1	53.4	180
2	5	1	30.5	30.8	197
-2	5	1	30.1	30.9	8
2	5	2	12.7	12.6	66
-2	5	2	13.3	13.5	121
2	5	3	15.7	14.9	83
-2	5	3	13.7	13.5	103
2	6	0	16.4	17.2	3
2	6	1	32.0	30.5	134
-2	6	1	28.2	27.0	236
2	6	2	6.6	6.9	260
-2	6	2	6.3	5.7	83
2	6	3	23.3	23.0	313
-2	6	3	18.6	18.7	72
2	7	0	21.1	19.4	4
2	7	1	31.4	31.8	179
-2	7	1	33.9	33.8	22
2	7	2	15.5	15.0	51
-2	7	2	16.8	15.8	135
2	7	3	21.0	20.8	315
-2	7	3	23.1	23.2	232
2	8	0	11.5	11.2	180
2	8	1	32.7	33.0	83
-2	8	1	33.4	33.7	289
2	8	2	9.2	9.5	92
-2	8	2	9.8	9.7	291
2	8	3	22.0	23.2	286
-2	8	3	21.8	22.8	99
2	9	0	10.0	9.8	177
2	9	1	22.2	22.5	196
-2	9	1	22.2	23.1	11
2	9	2	13.7	13.6	238
-2	9	2	12.8	12.8	306
2	10	0	1.3	1.2	18
2	10	1	3.2	3.0	35
-2	10	1	5.7	5.6	358
2	11	0	14.7	14.4	9
3	0	1	27.6	26.5	82
3	0	2	5.0	4.4	292
3	0	3	14.6	13.5	268
3	0	4	19.3	19.2	11
3	1	0	16.9	17.6	251
3	1	1	35.9	35.5	77
-3	1	1	38.8	38.8	284
3	1	2	7.7	7.9	299
-3	1	2	7.5	7.3	105
3	1	3	12.6	12.5	58
-3	1	3	8.9	9.2	326
3	1	4	7.1	7.0	256
-3	1	4	7.9	8.2	119
3	2	0	18.3	17.5	268
3	2	1	75.4	73.2	257
-3	2	1	77.6	76.3	291
3	2	2	47.8	47.0	178
-3	2	2	49.1	49.0	15
3	2	3	15.7	16.3	80
-3	2	3	16.7	17.4	109
3	2	4	18.4	18.1	352
-3	2	4	20.1	19.6	209
3	3	0	15.4	14.8	112
3	3	1	33.4	33.2	231
-3	3	1	30.0	30.4	134
3	3	2	40.7	40.9	325
-3	3	2	36.0	36.5	43
3	3	3	22.5	22.0	348
-3	3	3	24.5	24.0	28
3	3	4	6.0	6.3	230
-3	3	4	7.4	7.1	144
3	4	0	35.0	35.0	271
3	4	1	65.5	65.0	301
-3	4	1	63.2	63.0	248
3	4	2	18.5	18.9	126
-3	4	2	24.6	25.6	66
3	4	3	19.3	19.9	144
-3	4	3	19.2	19.7	48
3	5	0	29.2	29.4	102
3	5	1	21.9	21.9	83
-3	5	1	25.5	25.0	282
3	5	2	10.4	11.0	255
-3	5	2	12.4	12.9	129
3	5	3	9.8	9.9	324
-3	5	3	13.7	13.5	55
3	6	0	15.7	15.7	94
3	6	1	22.9	22.7	279
-3	6	1	24.7	24.3	280
3	6	2	30.0	30.3	197
-3	6	2	29.0	29.5	359
3	6	3	17.8	17.5	199
-3	6	3	15.7	15.7	350
3	7	0	18.6	17.2	107
3	7	1	13.7	12.7	168
-3	7	1	12.8	12.1	211
3	7	2	26.2	26.2	296
-3	7	2	24.0	24.3	78
3	7	3	17.8	17.3	36
-3	7	3	16.4	16.2	344
3	8	0	27.5	27.3	93
3	8	1	19.4	19.7	319
-3	8	1	16.9	17.2	244
3	8	2	21.7	21.5	239
-3	8	2	17.3	17.0	318
3	9	0	12.0	12.4	112
3	9	1	7.1	7.1	100
-3	9	1	9.6	9.5	278
3	9	2	15.6	15.4	278
-3	9	2	14.4	14.7	101
3	10	0	2.6	2.6	100
3	10	1	5.5	5.5	341
-3	10	1	4.3	4.4	274
4	0	0	112.0	114.0	185
4	0	1	10.8	11.0	268
4	0	2	21.8	22.0	10
4	0	3	2.1	2.3	65
4	0	4	20.6	21.6	5
4	1	0	11.8	12.6	3
4	1	1	68.7	66.3	208
-4	1	1	67.0	65.2	336
4	1	2	20.2	20.2	244
-4	1	2	25.2	25.1	316
4	1	3	4.8	4.5	327
-4	1	3	4.2	4.4	207
4	1	4	11.2	11.5	40
-4	1	4	17.0	17.0	156
4	2	0	56.7	58.4	188
4	2	1	59.6	57.9	152
-4	2	1	58.3	57.1	213
4	2	2	28.0	28.2	55
-4	2	2	22.9	21.9	321
4	2	3	11.1	11.1	273
-4	2	3	11.3	10.9	102
4	2	4	12.1	11.8	204
-4	2	4	12.9	12.7	155
4	3	0	15.7	14.3	180
4	3	1	44.0	43.4	59
-4	3	1	46.0	45.4	122
4	3	2	26.0	25.9	287
-4	3	2	24.7	24.6	275
4	3	3	9.9	10.0	320
-4	3	3	8.7	8.9	226
4	4	0	71.2	69.3	187
4	4	1	14.2	14.4	98
-4	4	1	15.1	15.0	268
4	4	2	31.1	31.3	342
-4	4	2	35.3	35.5	31
4	4	3	3.5	3.6	270
-4	4	3	4.1	3.9	123
4	5	0	21.1	20.8	3
4	5	1	25.4	24.8	239
-4	5	1	23.2	22.5	304
4	5	2	7.2	7.0	18
-4	5	2	2.5	2.7	83
4	5	3	16.6	16.9	169
-4	5	3	18.1	17.4	17
4	6	0	22.3	23.1	195
4	6	1	17.5	17.6	206
-4	6	1	15.8	15.5	164
4	6	2	8.8	9.1	169
-4	6	2	9.2	9.3	153
4	6	3	4.5	4.3	119
-4	6	3	5.7	5.8	234
4	7	0	21.9	21.7	179
4	7	1	9.3	9.1	114
-4	7	1	10.8	10.5	75
4	7	2	29.2	29.3	300
-4	7	2	26.2	26.4	258
4	8	0	42.2	42.1	189
4	8	1	20.0	19.8	154
-4	8	1	20.3	20.5	218
4	8	2	26.3	26.3	27
-4	8	2	25.4	25.7	351
4	9	0	9.4	9.3	177
4	9	1	13.1	12.8	339
-4	9	1	14.1	14.1	199
4	9	2	27.7	29.0	299
-4	9	2	25.0	25.9	258
4	10	0	35.2	36.2	189
4	10	1	4.3	4.2	127
-4	10	1	5.6	5.6	253
5	0	1	56.9	56.8	276
5	0	2	15.7	15.0	9
5	0	3	9.3	8.2	92
5	1	0	27.1	27.3	277
5	1	1	21.5	20.8	293
-5	1	1	16.6	16.5	64
5	1	2	27.0	27.6	100
-5	1	2	27.7	27.5	271
5	1	3	14.6	14.0	6
-5	1	3	15.6	15.1	24
5	2	0	31.0	29.5	93
5	2	1	36.2	36.7	293
-5	2	1	33.4	34.0	265
5	2	2	30.7	30.4	332
-5	2	2	32.5	32.4	218
5	2	3	8.4	8.4	94
-5	2	3	8.5	8.3	101
5	3	0	24.9	25.4	278
5	3	1	24.5	25.5	152
-5	3	1	27.2	28.4	221
5	3	2	4.5	4.3	80
-5	3	2	7.1	7.4	315
5	3	3	35.6	35.8	28
-5	3	3	32.8	33.2	347
5	4	0	13.5	13.3	269
5	4	1	26.4	25.9	266
-5	4	1	28.5	28.5	296
5	4	2	10.2	10.5	343
-5	4	2	11.7	12.0	220
5	4	3	6.5	6.6	104
-5	4	3	6.2	6.1	89
5	5	0	5.4	5.6	305
5	5	1	12.6	12.9	81
-5	5	1	16.5	16.7	281
5	5	2	8.3	8.1	64
-5	5	2	11.5	11.2	312
5	5	3	16.1	16.3	337
-5	5	3	19.6	19.3	44
5	6	0	29.0	30.2	95
5	6	1	22.7	23.0	282
-5	6	1	22.4	22.5	282
5	6	2	21.2	21.0	2
-5	6	2	21.0	20.4	192
5	6	3	9.6	9.7	301
-5	6	3	10.3	10.1	243
5	7	0	4.9	4.8	304
5	7	1	8.3	8.2	106
-5	7	1	12.1	12.4	265
5	7	2	4.8	4.9	252
-5	7	2	3.2	3.3	57
5	8	0	4.6	4.4	115
5	8	1	10.5	11.2	265
-5	8	1	13.8	13.8	310
5	8	2	8.2	8.3	233
-5	8	2	11.1	11.9	307
5	9	0	9.4	9.4	289
5	9	1	12.8	12.9	108
-5	9	1	16.0	16.3	261
6	0	0	7.4	7.3	348
6	0	1	21.2	22.1	277
6	0	2	25.5	25.3	180
6	0	3	19.1	19.6	104
6	1	1	25.2	25.7	358
-6	1	1	27.6	27.6	205
6	1	3	12.2	12.2	53
-6	1	3	13.5	13.4	123
6	2	0	9.9	10.5	191
6	2	1	21.7	22.6	276
-6	2	1	21.0	21.7	100
6	2	2	21.2	21.7	289
-6	2	2	22.1	22.4	76
6	2	3	26.5	25.9	143
-6	2	3	20.9	20.3	236
6	3	0	15.4	16.5	182
6	3	1	5.0	5.0	132
-6	3	1	6.2	5.8	293
6	3	2	14.2	14.9	299
-6	3	2	13.8	13.8	259
6	3	3	15.0	14.8	223
-6	3	3	13.8	13.7	330
6	4	0	45.8	46.6	183
6	4	1	33.9	33.4	311
-6	4	1	30.5	30.2	58
6	4	2	10.6	10.8	317
-6	4	2	10.6	11.1	59
6	4	3	23.6	23.4	85
-6	4	3	25.5	25.6	296
6	5	0	3.3	2.5	357
6	5	1	29.7	29.8	47
-6	5	1	24.7	24.8	152
6	5	2	4.5	4.6	267
-6	5	2	5.1	5.2	299
6	6	0	6.9	6.9	350
6	6	1	5.0	5.1	177
-6	6	1	9.0	9.1	196
6	6	2	2.8	2.7	198
-6	6	2	3.9	4.1	171
6	7	0	9.7	9.8	187
6	7	1	21.1	21.2	350
-6	7	1	25.1	25.4	211
6	7	2	12.5	13.2	303
-6	7	2	12.0	12.4	252
6	8	0	22.8	23.8	184
6	8	1	32.0	32.1	235
-6	8	1	33.0	33.0	136
6	9	0	14.2	14.8	1
7	0	1	18.7	19.1	99
7	0	2	4.4	4.0	124
7	0	3	11.2	11.0	278
7	1	0	8.6	8.4	306
7	1	1	5.0	4.9	221
-7	1	1	6.3	6.4	140
7	1	2	9.2	9.0	34
-7	1	2	13.1	12.9	340
7	1	3	8.4	8.2	290
-7	1	3	5.5	5.6	71
7	2	0	24.5	24.5	92
7	2	1	22.3	22.5	76
-7	2	1	23.8	24.8	117
7	2	2	35.5	35.6	356
-7	2	2	36.8	36.7	200
7	2	3	6.9	6.9	212
-7	2	3	8.7	8.6	334
7	3	0	24.6	25.3	282
7	3	1	26.1	26.1	77
-7	3	1	24.4	25.1	286
7	3	2	38.2	37.1	120
-7	3	2	36.2	35.8	251
7	3	3	6.0	5.9	225
-7	3	3	4.7	4.7	160
7	4	0	10.5	10.4	273
7	4	1	6.0	6.2	165
-7	4	1	4.0	3.9	62
7	4	2	14.0	13.7	17
-7	4	2	13.3	13.8	194
7	5	0	30.8	31.1	280
7	5	1	7.5	7.1	4
-7	5	1	5.8	6.0	12
7	5	2	5.1	5.1	105
-7	5	2	6.2	6.0	300
7	6	0	8.3	8.2	271
7	6	1	33.7	34.1	101
-7	6	1	34.4	34.5	91
7	6	2	12.8	13.0	17
-7	6	2	12.5	12.7	194
7	7	0	8.3	8.1	301
7	8	0	8.1	8.0	95
8	0	0	32.7	35.9	10
8	0	1	3.0	3.2	77
8	0	2	3.5	3.5	303
8	1	0	28.4	29.2	183
8	1	1	15.0	14.7	56
-8	1	1	13.0	12.8	137
8	1	2	20.4	20.3	61
-8	1	2	23.7	23.3	134
8	2	0	17.7	16.9	17
8	2	1	18.0	18.2	275
-8	2	1	18.3	18.4	96
8	2	2	14.8	15.1	189
-8	2	2	15.6	15.4	193
8	3	1	8.1	8.3	341
-8	3	1	9.3	9.2	222
8	3	2	1.8	1.0	79
-8	3	2	5.2	5.4	176
8	4	0	40.1	41.3	8
8	4	1	9.9	9.6	351
-8	4	1	8.2	8.2	22
8	4	2	12.8	12.4	240
-8	4	2	10.1	9.7	148
8	5	0	7.8	7.9	188
8	5	1	5.1	5.0	301
-8	5	1	7.3	7.3	252
8	5	2	8.6	8.9	103
-8	5	2	8.7	8.7	113
8	6	0	12.6	11.9	24
8	6	1	9.7	9.4	319
-8	6	1	9.4	9.3	57
8	7	0	10.9	10.5	190
9	0	1	36.0	34.0	99
9	0	2	2.9	2.9	199
9	1	0	4.6	4.4	257
9	1	1	9.1	9.6	298
-9	1	1	12.6	12.6	75
9	1	2	8.5	8.7	188
-9	1	2	11.1	11.1	179
9	2	0	12.0	11.7	274
9	2	1	19.2	19.0	111
-9	2	1	18.3	18.1	93
9	2	2	4.9	5.0	157
-9	2	2	5.5	5.7	39
9	3	0	10.3	10.6	99
9	4	0	3.9	3.9	80
9	4	1	11.3	11.1	107
-9	4	1	11.3	11.4	110
9	5	0	12.1	11.4	98
10	0	0	21.8	22.0	8
10	0	1	12.0	12.7	99
10	1	0	7.5	7.6	183
10	1	1	22.6	22.4	173
-10	1	1	24.3	24.0	24
10	2	0	2.3	2.3	31

ameters from the refinements of the two complete sets of data are used in the following discussion and are shown in Fig. 5. Some oxygen–oxygen distances are given in Fig. 6. Standard deviations of results are listed in the caption for Fig. 5. The maximum deviations between the results for the two sets of data are 0·029 Å [C(1)O(2)] and 2·4° [∠O(1)C(1)C(2)] for bonds and angles not involving hydrogen atoms.

A consideration of distances in the three carboxyl groups indicates quite unambiguously that in this particular crystalline form the central carboxyl group is the one which is ionized and not the carboxyl group adjacent to the hydroxyl group. The carbon–oxygen distances (with estimated standard deviations of about 0·007 Å) are 1·263 and 1·253 Å for the central carboxyl group, 1·218 and 1·301 Å for the terminal carboxyl

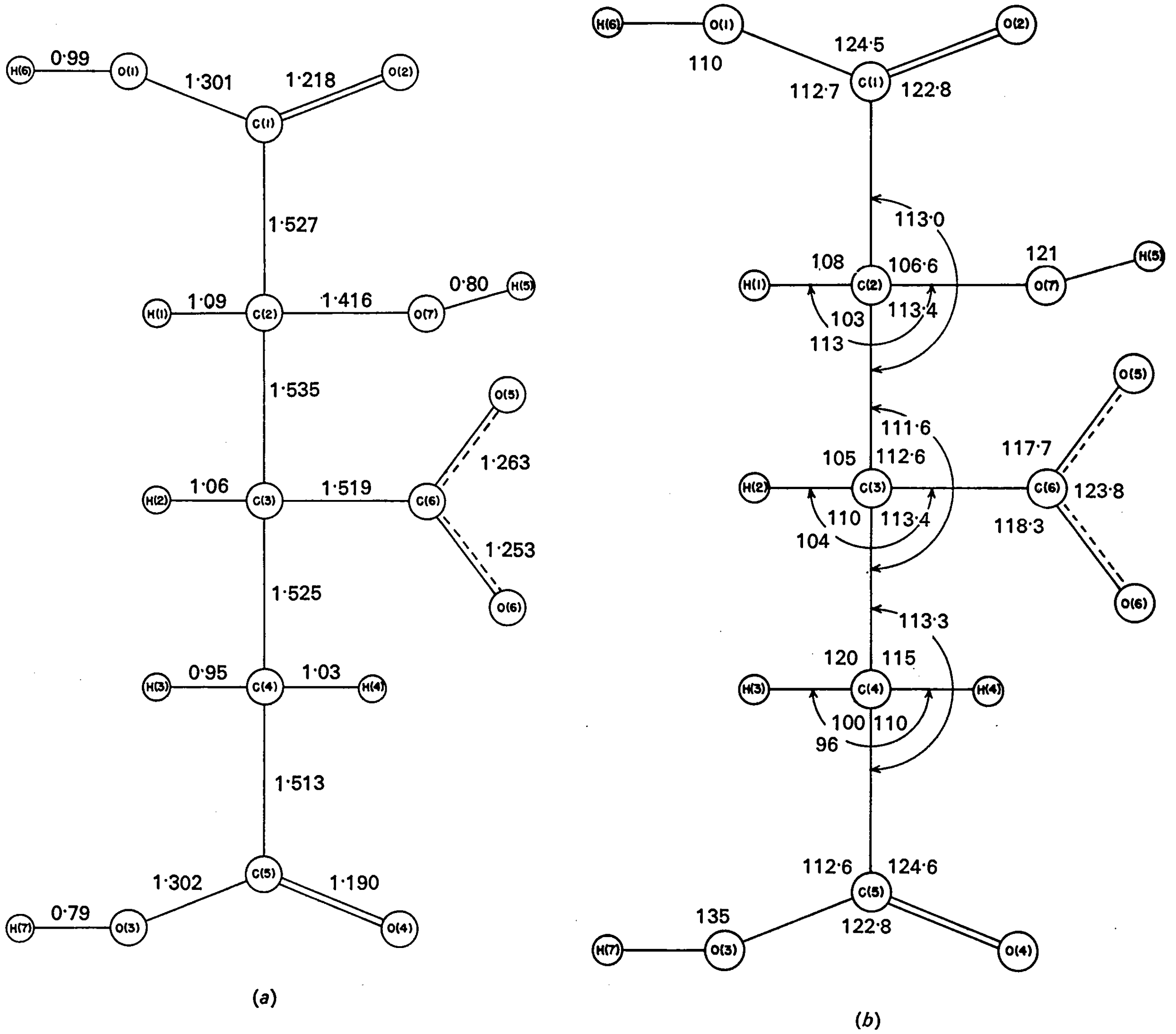
Table 7. *Values of anisotropic temperature factors along the principal axes*

Values of the temperature factors (Å^2) along the major, intermediate and minor axes of the thermal ellipsoids are given together with the direction cosines of these axes with respect to the axes of the crystallographic unit cell. Results are listed first for the Cu–Mo data and then for the Cr data.

	Cu–Mo data				Cr data			
	B	l_1	l_2	l_3	B	l_1	l_2	l_3
K	5·69	0·618	0·382	−0·687	6·18	0·644	0·388	−0·659
	2·96	0·682	0·174	0·710	3·26	0·655	0·166	0·738
	1·75	0·390	−0·908	−0·153	1·95	0·395	−0·907	−0·147
O(1)	5·00	−0·616	0·030	−0·787	5·15	−0·670	−0·110	−0·734
	2·10	0·127	0·990	−0·061	2·32	−0·016	0·991	−0·135
	1·84	0·777	−0·138	−0·614	1·57	0·742	−0·079	−0·665
O(2)	3·53	0·479	0·064	0·875	4·16	0·531	0·061	0·845
	2·27	0·674	−0·666	−0·320	3·21	0·843	0·064	−0·534
	2·00	0·563	0·743	−0·362	1·36	−0·086	0·996	−0·018
O(3)	11·45	0·737	−0·034	0·675	12·59	0·788	−0·049	0·614
	3·45	−0·583	0·473	0·660	3·94	−0·563	0·348	0·750
	1·50	−0·342	−0·880	0·329	1·87	−0·250	−0·936	0·246
O(4)	5·48	0·755	−0·105	0·647	6·25	0·898	−0·056	0·437
	3·31	−0·653	−0·214	0·727	3·94	−0·416	−0·436	0·798
	2·54	0·062	−0·971	−0·230	2·56	0·146	−0·898	−0·415
O(5)	3·41	0·325	−0·488	−0·810	3·44	−0·519	0·355	0·778
	2·15	−0·335	0·741	−0·581	2·42	0·409	−0·696	0·590
	2·00	0·884	0·460	0·077	1·74	0·751	0·625	0·216
O(6)	3·05	0·865	−0·257	−0·430	2·86	0·986	−0·138	0·097
	2·52	0·499	0·373	0·782	2·73	0·030	0·712	0·702
	1·54	−0·040	−0·891	0·452	1·78	−0·166	−0·689	0·706
O(7)	3·95	0·931	0·189	0·312	4·42	0·874	0·378	0·306
	2·25	−0·076	0·937	−0·342	3·19	−0·280	0·906	−0·317
	1·67	−0·357	0·295	0·887	1·89	−0·397	0·191	0·898
C(1)	2·49	−0·018	−0·543	—0·840	3·17	0·185	0·671	−0·718
	1·70	−0·115	0·835	−0·538	1·98	−0·542	0·679	0·496
	1·61	0·993	0·087	−0·077	1·64	0·820	0·297	0·489
C(2)	2·37	0·479	0·549	0·684	3·01	0·604	0·320	0·730
	2·07	0·863	−0·437	−0·254	2·64	−0·400	−0·670	0·625
	1·82	0·160	0·712	−0·684	1·29	0·689	−0·670	−0·277
C(3)	2·35	0·000	0·969	0·247	2·89	0·976	−0·195	−0·094
	2·02	−0·422	−0·224	0·878	2·16	−0·002	−0·445	0·895
	1·52	0·907	−0·104	0·409	1·56	−0·216	−0·874	−0·435
C(4)	2·87	−0·524	0·477	0·705	3·14	0·529	−0·742	−0·412
	2·57	0·823	0·072	0·563	2·79	0·848	0·477	0·230
	1·93	0·218	0·876	−0·431	1·81	0·026	−0·471	0·882
C(5)	4·76	0·239	0·108	0·965	4·38	0·655	0·181	0·734
	2·65	0·918	0·299	−0·261	2·93	0·736	−0·375	−0·564
	1·71	−0·317	0·948	−0·027	1·84	0·173	0·909	−0·378
C(6)	2·17	−0·513	−0·511	0·689	2·97	0·913	0·403	−0·063
	1·94	0·810	−0·555	0·191	2·49	−0·406	0·883	−0·237
	1·60	0·285	0·656	0·699	1·15	−0·040	0·242	0·969

group adjacent to the hydroxyl group and 1·190 and 1·302 Å for the terminal carboxyl group adjacent to the methylene group. The last distance is somewhat uncertain because the oxygen atom O(3) is probably disordered. There is a very short hydrogen bond 2·516 Å with $O(5^{vi})$ as acceptor and O(1) as donor and the distance of the H(6) to $O(5^{vi})$ is 1·53 Å and to O(1) is 0·99 Å (see Table 9 for the meaning of the superscripts). A concerted movement of all H(6) back and forth over the presumably low potential barrier in the short hydrogen bond can determine whether the terminal carboxyl group (adjacent to the hydroxyl group) or the central group is the one which is ionized. In the potassium salt of isocitric lactone (Glusker *et al.*, 1963) there is a short hydrogen bond (2·49 Å) between adjacent ions involving the same two carboxyl groups (*i.e.* those nearest and next nearest to the hydroxyl group). However the structure of the lactone was determined from two-dimensional data and the hydrogen atom position could not be located exactly from a difference Fourier synthesis since it appeared as an elongated blur along the oxygen–oxygen direction.

All carbon–carbon bonds lie in the range 1·513–1·535 Å and the long carbon–carbon bond of 1·55 Å found between the hydroxyl group and the central carboxyl group in the citrate ion in sodium dihydrogen citrate and trimagnesium dicitrate (Glusker, van der Helm, Love, Dornberg, Minkin, Johnson & Patterson,



(*a*) (*b*)

Fig. 5. (*a*) Covalent bond lengths (Å) and (*b*) angles (°) for the isocitrate ion. Standard deviations of results are: Bond lengths K–O, 0·005 Å; C–O, C–C, O···O, 0·007 Å; C–H, O–H, 0·1 Å. Interbond angles O–K–O, 0·2°; O–C–O, O–C–C, C–C–C, 0·5°; H–C–C, H–O–C, H–C–O, 5°; H–C–H, 7°.

Table 8. *Equations of some least-squares planes in the isocitrate ion and perpendicular distances of certain atoms from these planes*

Equations are expressed in the form:

$$lX+mY+nZ=D$$

where distances, D, and coordinates X, Y and Z are expressed in Å. The deviations, Δ, from these planes are also expressed in Å.

Designation of plane	Atoms in plane	l	m	n	D
(1)	O(1), O(2), C(1), C(2)	0·8018	0·0017	0·5975	3·9262
(2)	O(3), O(4), C(5), C(4)	−0·8587	0·3194	−0·4007	−3·0046
(3)	O(5), O(6), C(6), C(3)	0·3419	−0·5499	−0·7621	−3·3190
(4)	C(2), C(3), C(4)	0·7647	−0·6312	−0·1298	−0·0445
(5)	C(1), C(2), C(3)	0·7130	−0·6956	0·0875	0·1543
(6)	C(3), C(4), C(5)	0·9338	−0·2837	0·2189	3·1609

Atoms	$\Delta(1)$	Atoms	$\Delta(2)$	Atoms	$\Delta(3)$	Atoms	$\Delta(4)$
O(1)	−0·007	O(3)	0·002	O(5)	−0·008	C(2)	0·000
O(2)	−0·005	O(4)	0·002	O(6)	−0·009	C(3)	0·000
C(1)	0·018	C(5)	−0·004	C(6)	0·024	C(4)	0·000
C(2)	−0·005	C(4)	0·001	C(3)	−0·007		
H(6)	−0·03	H(7)	0·20	$H(5^{xi})$	−1·40	C(1)	−0·332
$O(5^{vi})$	−0·084	$O(1^{vii})$	1·572	$O(7^{xi})$	−1·947	C(5)	−0·698
$H(7^{x})$	−1·23	$O(6^{viii})$	−1·527	$H(6^{xii})$	−0·28	C(6)	1·095
$O(3^{x})$	−1·033			$O(1^{xii})$	−0·350		

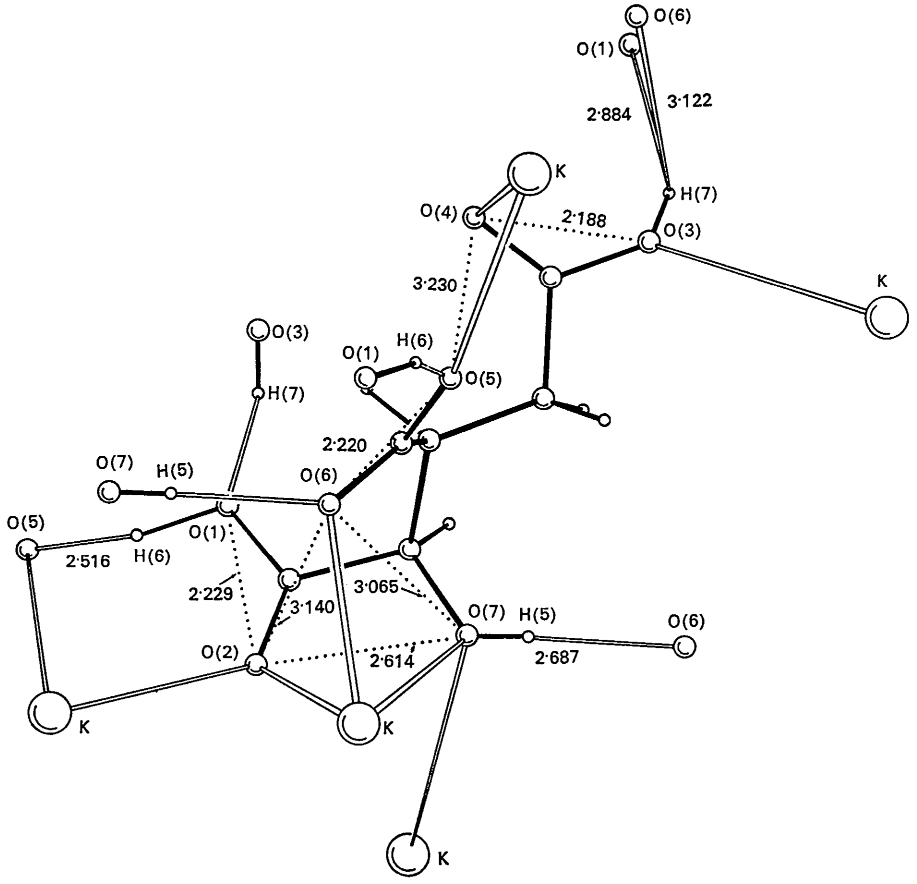


Fig. 6. Some oxygen–oxygen and potassium–oxygen distances in the ion and its surroundings.

1965; Johnson, 1965) is not present. However the bond C(1)–C(2) is longer than C(4)–C(5) in the isocitrate ion. The oxygen–oxygen distance between the carboxyl group and the α-hydroxy group is short, 2·622 Å, as found for other citrates (Glusker *et al.*, 1965), and the hydroxyl oxygen atom is 0·071 Å out of the plane of the terminal carboxyl group.

The carbon backbone of the ion C(1)C(2)C(3)C(4)-C(5) is extended, as shown in Figs. 4 and 6, with C(1) 0·332 Å and C(5) 0·698 Å from the plane through C(2)C(3)C(4). The central carboxyl group is slightly inclined to this plane; the perpendicular distances of O(5) and O(6) from the plane C(2)C(3)C(4) are nearly the same (1·520 and 1·458 Å). Deviations of atoms from certain planes in the molecule are listed in Table 8.

All three available hydrogen atoms are involved in hydrogen bonding (see Table 9). There are no intramolecular hydrogen bonds. The very short hydrogen bond O(1)–H(6)---O(5$^{\mathrm{vi}}$), 2·516 Å has already been mentioned; the ions involved are related by the screw axis parallel to the *a* axis. The hydrogen atom H(5), of the hydroxyl group forms a hydrogen bond to O(6$^{\mathrm{v}}$) of another ion related to it by a *c* translation with the distance O(6$^{\mathrm{v}}$)---O(7) equal to 2·687 Å. The third hydrogen atom H(7), is attached to O(3). In Table 7 it can be seen that O(3) is very anisotropic, which may mean that it is disordered. The nearest neighbors in other molecules to O(3) are O(1$^{\mathrm{vii}}$) at 2·884 Å, O(6$^{\mathrm{viii}}$) at 3·122 Å and O(2$^{\mathrm{ix}}$) at 3·196 Å (see Table 9). Of these three oxygen atoms O(1$^{\mathrm{vii}}$) and O(6$^{\mathrm{viii}}$) are in good positions to accept a hydrogen bond from O(3) and it must be concluded that this might be a cause of disorder. As the value of the temperature factor along the major principal axis is 12 Å^2 it may be assumed that there are two possible locations of O(3), designated O(3^{a}) and O(3^{b}), displaced along this direction. If this displacement O(3^{a})---O(3^{b}) is 0·5 Å (corresponding approximately to the displacement for $B = 12$ Å^2) the hydrogen bond O(3^{a})---O(1$^{\mathrm{vii}}$) is shortened to 2·84 Å and the hydrogen bond O(3^{b})---O(6$^{\mathrm{viii}}$) is shortened

Table 9. *Hydrogen bonds*

Donor (O*d*)	Hydrogen	Acceptor (O*a*)	O*d*---O*a* (Å)	H—O*d* (Å)	H---O*a* (Å)	∠O*a*---H—O*d* (°)	∠H—O*d*---O*a* (°)	∠H—O*d*—C (°)	∠O---O—C (°)
O(7)	H(5)	O(6$^{\mathrm{v}}$)	2·687	0·80	1·90	167	9	121	121·0
O(1)	H(6)	O(5$^{\mathrm{vi}}$)	2·516	0·99	1·53	170	6	109	115·8
O(3)	H(7)	O(1$^{\mathrm{vii}}$)	2·884	0·79	2·28	133	35	135	101·9

Parameters

O(3$^{\mathrm{a}}$) at 0·4391, 0·5450, 0·2595
O(3$^{\mathrm{b}}$) at 0·4728, 0·5429, 0·3298

With respect to the coordinates in Table 3 the ions are designated:

Superscript		Superscript		Superscript	
none	x, y, z	v	$x, y, z-1$	x	$\frac{1}{2}-x, 1-y, \frac{1}{2}+z$
i	$\frac{1}{2}-x, -y, z-\frac{1}{2}$	vi	$x-\frac{1}{2}, \frac{1}{2}-y, 2-z$	xi	$x, y, 1+z$
ii	$1-x, y-\frac{1}{2}, -z+1\frac{1}{2}$	vii	$\frac{1}{2}-x, 1-y, z-\frac{1}{2}$	xii	$\frac{1}{2}+x, \frac{1}{2}-y, 2-z$
iii	$1-x, y-\frac{1}{2}, -z+\frac{1}{2}$	viii	$1-x, y+\frac{1}{2}, 1\frac{1}{2}-z$		
iv	$\frac{1}{2}-x, -y, z+\frac{1}{2}$	ix	$\frac{1}{2}+x, \frac{1}{2}-y, 1-z$		

Table 10. *Some distances and angles in the polyhedra of oxygen atoms surrounding the potassium ions*

(*a*) Potassium ion–oxygen atom distances (Å).

K---O(2$^{\mathrm{i}}$)	2·725
O(5$^{\mathrm{ii}}$)	2·726
O(6)	2·771
O(7)	2·799
O(2)	2·814
O(4$^{\mathrm{ii}}$)	3·058
O(3$^{\mathrm{iii}}$)	3·158
O(7$^{\mathrm{iv}}$)	3·225

(*b*) Oxygen–oxygen distances (Å).

	O(2$^{\mathrm{i}}$)	O(5$^{\mathrm{ii}}$)	O(6)	O(7)	O(2)	O(4$^{\mathrm{ii}}$)	O(3$^{\mathrm{iii}}$)
O(7$^{\mathrm{iv}}$)	3·67	3·57	5·26	5·07	3·43	5·71	5·98
O(3$^{\mathrm{iii}}$)	3·20	3·97	4·47	3·41	5·29	3·36	
O(4$^{\mathrm{ii}}$)	5·01	3·23	3·55	4·94	5·56		
O(2)	4·06	5·24	3·14	2·62			
O(7)	3·43	5·31	3·07				
O(6)	5·22	5·13					
O(5$^{\mathrm{ii}}$)	3·33						

to 2·91 Å. Of course, if O(3) is disordered, there must also be disorder in H(7) and in at least one other atom in the planar –C–COOH group.

It is difficult to state how many oxygen atoms are in significant contact with the potassium ions. Data on the coordination are listed in Table 10. The structure, shown in Fig. 7, consists of columns of pairs of potassium ions surrounded by oxygen atoms, the six closest of which are at distances 2·725–3·058 Å. These six are composed of O(6), O(7), O(2) in one isocitrate ion, O(2) in another ion, and O(5) and O(4) in a third ion. Oxygen atom O(1) is not in contact with the potassium ion. Each isocitrate ion forms a tridentate chelate with one potassium ion involving 5-, 6- and 7-membered rings [KO(2)C(1)C(2)O(7), KO(7)C(2)C(3)C(6)O(6) and KO(2)C(1)C(2)C(3)C(6)O(6)] and a bidentate chelate with another potassium ion involving a seven-membered ring [KO(5)C(6)C(3)C(4)C(5)O(4)]. Two polyhedra of oxygen atoms are shared between two potassium ions related by approximately a translation of $\frac{1}{4}a$ and these polyhedra are also linked in the c direction, in both cases O(2) being the shared oxygen.

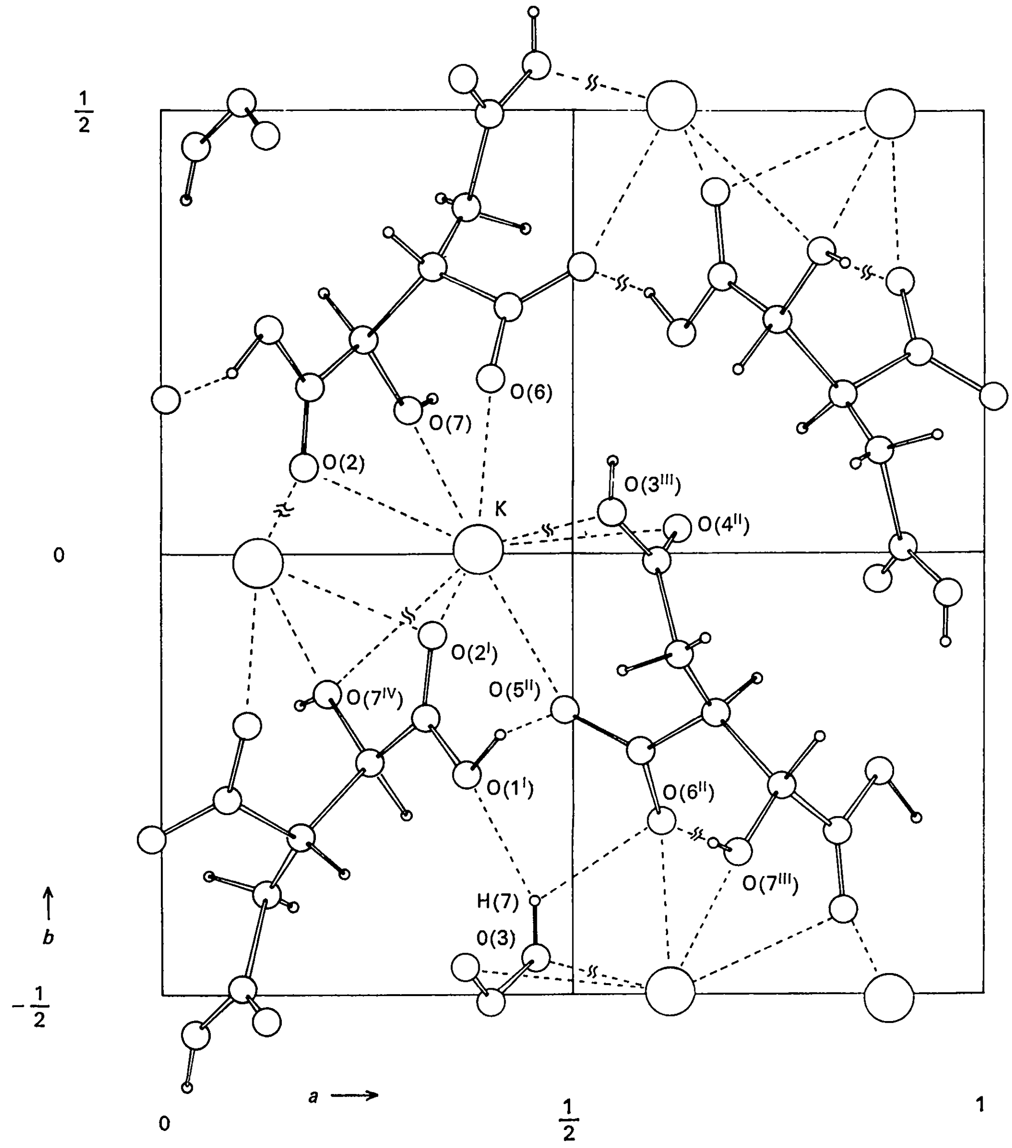


Fig. 7. Projection of the structure in the (−)c direction showing the coordination of oxygen atoms round the potassium ions and the hydrogen bond system. Hydrogen bonds to molecules translated in the **c** direction are indicated by a break in the dotted line.

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References

CAHN, R. S., INGOLD, C. & PRELOG, V. (1966). *Angew. Chem. internat. Edit.* **5**, 385.
GLUSKER, J. P., PATTERSON, A. L., LOVE, W. E. & DORNBERG, M. L. (1963). *Acta Cryst.* **16**, 1102.
GLUSKER, J. P., VAN DER HELM, D., LOVE, W. E., DORNBERG, M. L., MINKIN, J. A., JOHNSON, C. K. & PATTERSON, A. L. (1965). *Acta Cryst.* **19**, 561.
International Tables for X-ray Crystallography (1962*a*). Vol. III, p. 202. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1962*b*). Vol. III, p. 213. Birmingham: Kynoch Press.
JOHNSON, C. K. (1965). *Acta Cryst.* **18**, 1004.
OKAYA, Y. & PEPINSKY, R. (1956). *Phys. Rev.* **103**, 1645.
PATTERSON, A. L., JOHNSON, C. K., VAN DER HELM, D. & MINKIN, J. A. (1962). *J. Amer. Chem. Soc.* **84**, 309.
PATTERSON, A. L. (1963). *Acta Cryst.* **16**, 1255.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
ZACHARIASEN, W. H. (1963*a*). *Acta Cryst.* **16**, 1139.
ZACHARIASEN, W. H. (1963*b*). Paper G-2, Amer. Cryst. Assn. Meeting, M.I.T., Cambridge, Mass., March 28–30.

Acta Cryst. (1968). B **24**, 592

Space Groups of Some *N*-Substituted 2-Halogenoalkylammonium Halides

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The space groups are reported of sixteen salts, one of which is dimorphous. A detailed study was subsequently made of the structure of one of them, 2-bromo-2-*p*-tolylethyldimethylammonium bromide.

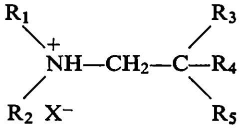
These compounds are of interest medically as adrenomotor antagonists (*e.g.*, Graham, 1962), and it was hoped that this crystallographic study would provide some correlation between molecular conformation and pharmacological activity.

Experimental

In an attempt to obtain better crystals, many of the compounds were recrystallized from analytical reagent grade methanol, ethanol or isopropyl alcohol. The alcohol was previously carefully dried with quicklime, as any water present would hydrolyse the halide to the corresponding alcohol. The densities were measured by

Table 1. *Chemical constitution of compounds described*

General formula:



$$R_1R_2\overset{+}{N}H\text{—}CH_2\text{—}CR_3R_4R_5\ X^-$$

Trivial name	R_1	R_2	R_3	R_4	R_5	X^-
Dibenamine	Benzyl	Benzyl	Cl	H	H	Cl^-
W	Cyclohexyl	Cyclohexyl	Cl	Methyl	H	Cl^-
U	Cyclohexyl	Cyclohexyl	Br	Methyl	H	Br^-
AT3	9-Fluorenyl	Ethyl	I	H	H	I^-
L13	n-Propyl	H	Br	Phenyl	H	Br^-
L17	Benzyl	H	Br	Phenyl	H	Br^-
L42	Methyl	Methyl	Br	Phenyl	Methyl	Br^-
SM	Methyl	Methyl	Br	4-Methylphenyl	H	Br^-
S2	Methyl	Methyl	Br	4-Chlorophenyl	H	Br^-
S4	Methyl	Methyl	Cl	3,4-Dichlorophenyl	H	Cl^-
S14	Methyl	Methyl	Br	3-Bromophenyl	H	Br^-
S15	Methyl	Methyl	Br	3-Chlorophenyl	H	Br^-
S1	Methyl	Methyl	Cl	4-Chlorophenyl	H	Cl^-
LT	Morpholine*		Cl	Phenyl	H	Cl^-
L23	Pyrrolidine*		Br	Phenyl	H	Br^-
R	Piperidine*		Br	Phenethyl	H	Br^-

* NHR_1R_2

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