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The Structure and Absolute Configuration of the Calcium Salt of Hibiscus Acid, the Lactone of (+)-*allo*-Hydroxycitric Acid

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The calcium salt of the lactone of (+)-*allo*-hydroxycitric acid crystallizes in the orthorhombic system as a tetrahydrate. The-unit cell dimensions are $a = 8·409 \pm 0·007$, $b = 21·232 \pm 0·012$, $c = 6·245 \pm 0·004$ Å. The observed and calculated densities are 1·80 and 1·79 g.cm^{-3} respectively. The space group is $P2_12_12_1$ with four units of $Ca(C_6O_7H_4).4H_2O$ per cell. 1412 independent data, of which 29 were below the threshold of measurement were collected on a manual diffractometer with Cu $K\alpha$ radiation by the θ–2θ scan technique (to $2\theta = 160°$). The structure was solved by heavy atom techniques and refined by full-matrix least squares to an R value of 0·056. All except three hydrogen atoms were found from a difference map and their parameters were refined. The absolute configuration of the free (+)-*allo*-hydroxycitric acid was determined, from anomalous dispersion measurements, to be 1*S*:2*R*-1,2-hydroxy-1,2,3-propanetricarboxylic acid. The two carboxyl groups are *trans* with respect to the plane of the lactone ring and the two $-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{COO}^-$ groupings are each almost planar. The lactone forms a bidentate chelate with the calcium ion. Two of the oxygen atoms of water molecules are markedly anisotropic indicating possible disorder. These lie in tunnels parallel to the c axis through the crystal and are probably lost as the crystal effloresces. The calcium ion is surrounded by nine oxygen atoms in a square antiprism arrangement with an additional square pyramid on one side. Calcium–oxygen distances vary from 2·41–2·64 Å.

Crystals of the calcium salt of hibiscus acid, the lactone of (+)-*allo*-hydroxycitric acid, were provided us by Dr Y. S. Lewis of the Central Food Technological Research Institute, Mysore, India. The acid was extracted from the calyxes of *Hibiscus sabdariffa* (Lewis & Neelakantan, 1965). This X-ray crystallographic study was made to determine the absolute configurations of the *allo*-hydroxycitric acids. The study was also made in order to determine the nature of the coordination of oxygen atoms around the calcium ion and to compare the absolute configuration and the packing with that of the calcium salt of the lactone of (−)-hydroxycitric acid (garcinia acid) (Glusker, Minkin, Casciato & Soule, 1969; Glusker, Minkin & Casciato, 1971).

Experimental

The crystals are orthorhombic. Cell dimensions were measured both from precession photographs and on a General Electric XRD-5 diffractometer with copper radiation [$\lambda(K\alpha_1) = 1·5405$ Å] as $a = 8·409 \pm 0·007$, $b = 21·232 \pm 0·012$, $c = 6·245 \pm 0·004$ Å. The space group is $P2_12_12_1$ (from the systematic absences $h00$ when h odd, $0k0$ when k odd and $00l$ when l odd) and $Z = 4$. The observed density is 1·80 g.cm^{-3} measured by flotation in a mixture of methylene iodide and carbon tetrachloride. The density, calculated for four units of $Ca(C_6O_7H_4).4H_2O$, is 1·79 g.cm^{-3}. The crystals deteriorated with time and became powdery, presumably due to some efflorescence.

Data were collected on two crystals, one a sphere of radius 0·17 mm. and the second a chunk 0·11 mm in radius and 0·40 mm in height. Intensities were measured with a General Electric XRD-5 manual diffractometer with the θ-2θ scan technique and with nickel-filtered copper radiation. The scan range and the 2θ values for background measurements were determined by inspection of the graphical trace of the peak. Of the 1412 reflections recorded 29 were below the threshold of measurement. The data were corrected for the Lorentz and polarization factors. Absorption factors were applied ($\mu = 53·1$ cm^{-1}). For the first crystal a spherical absorption correction was applied and for the second a correction for the ellipsoid of revolution (Johnson, 1963).

Solution of the structure

The position of the calcium ion was determined from the $|F|^2$ map. Since the value of x is approximately 0·75 for this heavy atom, the solution of the structure was difficult because there was symmetry at $x = \frac{1}{4}$ and $x = \frac{3}{4}$ in Fourier maps. The structure was eventually determined by the vector superposition method with the four calcium ion positions as successive origins for the $|F|^2$ map. The initial R value for the structure so derived was 0·39.

After two cycles of block diagonal isotropic least squares calculations a Fourier map was computed. This indicated that the positions of two water mole-

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cules were not correct. When these were corrected the R value was 0·22. This dropped to 0·104 after four cycles of isotropic least-squares calculation and to 0·074 after three cycles of block diagonal anisotropic least squares.

Absolute configuration

The absolute configuration of the lactone ion was established by a measurement of Friedel-related pairs of reflections on the General Electric XRD-5 diffractometer with copper $K\alpha$ radiation. For the calcium ion with copper radiation $\Delta f' = +0{\cdot}341$ and $\Delta f'' = 1{\cdot}286$ (Cromer & Liberman, 1970). A comparison of experimental values of the ratio $(I_+ - I_-)/(I_+ + I_-)$ and computed values* of D/S (Patterson, 1963) have already been listed (Glusker, Minkin, Casciato & Soule, 1969) for the 15 highest of these ratios measured in 78 randomly chosen pairs of reflections. Of these 78 pairs of reflections 58 pairs had differences in intensities which were greater than $2\frac{1}{2}$ times the standard deviation of the measurement of one reflection. The observed and calculated ratios had the same sign for each of these 58 pairs. This means that the absolute configuration, in the Cahn–Ingold notation (Cahn, Ingold & Prelog, 1966) corresponds to (1*S*:2*R*)-1,2-hydroxy-1,2,3-propane-tricarboxylic acid (or 2*S*:3*R*-2-hydroxycitric acid) for the free (+)-*allo*-hydroxycitric acid. This had also been deduced from chemical studies (Lewis & Neelakantan, 1965; Boll, Sørensen & Balieu, 1969). These studies included the application of Hudson's lactone rule, relative pK values, nuclear magnetic resonance and infrared spectra, ORD and CD curves and a calculation of partial molar rotations. The assignment was confirmed visually by taking a first and second level integrated Weissenberg photograph ($hk1$ and $hk2$) with chromium radiation. $\Delta f' = -0{\cdot}221$, $\Delta f'' = 2{\cdot}514$ for the calcium ion with chromium radiation (Cromer & Liberman, 1970). The intensity differences of certain Friedel-related reflections were clearly visible on the photograph.

Refinement of the structure

The measured data were corrected for anomalous dispersion by the method of Patterson (1963) to give structure factors free of this effect. At this stage ($R = 0{\cdot}074$) a difference map was calculated. The positions of nine of the twelve hydrogen atoms were clearly revealed, those attached to the carbon atoms of the lactone ring being the highest peaks. Further refinement by block-diagonal least squares with these positions for hydrogen atoms gave $R = 0{\cdot}061$. An extinction correction was applied (Zachariasen, 1963*a*) in the form $F_{\rm corr} = F_{\rm obs}[1 + \alpha\beta_{(2\theta)}{\rm Lp}|F_{\rm obs}|^2]$ with $\alpha = 5{\cdot}3 \times 10^{-6}$ (determined graphically). Values of $\beta_{(2\theta)}$ listed by Zachariasen (1963*b*) were used.

Table 1. *Final parameters of atoms*

Positional parameters are expressed as fractions of cell edges. There for the nonhydrogen atoms are multiplied by 10^4 and those for the hydrogen atoms by 10^3. Anisotropic temperature factors are expressed as

$$\exp\,[-\tfrac{1}{4}(B_{11}h^2a^{*2} + \cdots + 2B_{12}hka^*b^* + \cdots) \times 10^{-2}]$$

and isotropic temperature factors as

$$\exp\,[(-B\sin^2\theta/\lambda^2) \times 10^{-2}]$$

with B values given in Å^2. Estimated standard deviations, determined from the inverted full matrices, are listed beside each parameter, with respect to the last decimal place given.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ca	7404 (1)	1999 (1)	0513 (2)	112 (4)	160 (4)	161 (4)	−16 (3)	−7 (4)	−3 (3)
O(1)	6394 (6)	1026 (2)	2701 (9)	235 (19)	275 (20)	302 (21)	−31 (16)	+74 (18)	−35 (17)
O(2)	5534 (6)	1942 (2)	3893 (8)	228 (15)	165 (15)	223 (17)	−44 (14)	−38 (15)	+64 (13)
O(3)	4065 (7)	−0463 (2)	7295 (11)	399 (25)	144 (16)	424 (26)	−37 (16)	−8 (23)	+39 (17)
O(4)	4293 (5)	0362 (2)	5130 (7)	217 (16)	169 (15)	214 (17)	−44 (13)	+8 (13)	−39 (13)
O(5)	4691 (5)	2181 (2)	9429 (7)	129 (13)	151 (13)	180 (16)	−6 (11)	−9 (14)	−48 (12)
O(6)	2396 (5)	1908 (2)	7984 (8)	105 (13)	214 (15)	303 (18)	+15 (13)	−5 (15)	−42 (14)
O(7)	6235 (5)	1231 (2)	8046 (7)	118 (14)	173 (15)	187 (16)	+9 (13)	−17 (13)	−46 (13)
O(*W*1)	2465 (7)	2432 (2)	2955 (8)	226 (18)	308 (19)	204 (17)	+93 (17)	+11 (19)	−12 (15)
O(*W*2)	8029 (9)	0238 (3)	7304 (22)	455 (32)	300 (26)	1526 (86)	+221 (24)	−340 (47)	−151 (42)
O(*W*3)	9378 (7)	1720 (3)	3367 (13)	241 (22)	386 (27)	603 (36)	−72 (21)	−155 (25)	+189 (26)
O(*W*4)	9470 (7)	1387 (3)	8605 (18)	174 (20)	395 (27)	1320 (70)	−114 (20)	+239 (32)	−392 (39)
C(1)	5502 (7)	1348 (3)	3833 (10)	172 (21)	227 (22)	139 (20)	−31 (18)	−29 (18)	+6 (17)
C(2)	4264 (6)	1045 (3)	5275 (10)	103 (18)	170 (19)	157 (20)	−16 (15)	−22 (17)	−19 (16)
C(3)	4584 (6)	1185 (2)	7669 (9)	125 (18)	118 (18)	161 (21)	+6 (15)	+19 (16)	−2 (16)
C(4)	3859 (8)	0603 (3)	8740 (11)	210 (22)	146 (20)	245 (24)	−17 (17)	+25 (20)	+31 (18)
C(5)	4089 (8)	0104 (3)	7052 (13)	184 (22)	185 (21)	348 (31)	−5 (18)	−28 (22)	−70 (22)
C(6)	3830 (7)	1805 (3)	8394 (9)	143 (19)	164 (19)	163 (20)	+25 (16)	+13 (17)	+24 (16)

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* where

$$D = \tfrac{1}{2}\{|F_+|^2 - |F_-|^2\} = \frac{-2\Delta f''}{f_d}(AB_d - BA_d)$$

$$S = \{\tfrac{1}{2}|F_+|^2 + |F_-|^2\} =$$

$$A^2 + B^2 + \frac{2\Delta f'}{f_d}(AA_d + BB_d) + \{(\Delta f')^2 + (\Delta f'')^2\}(A_d^2 + B_d^2)/f_d^2.$$

A, B for structure with no anomalous dispersion, A_d, B_d for the anomalous scatterer.

Table 1 (*cont.*)

	x	y	z	B
H(1)	350 (12)	115 (4)	519 (17)	3 (2)
H(2)	450 (9)	051 (4)	1011 (13)	1 (1)
H(3)	263 (12)	070 (5)	885 (18)	4 (2)
H(4)	666 (14)	094 (5)	766 (23)	6 (3)
H($W1a$)	214 (15)	252 (6)	368 (22)	6 (4)
H($W1b$)	339 (14)	226 (5)	266 (20)	4 (3)
H($W2a$)	815 (10)	−005 (4)	784 (15)	3 (2)
H($W3a$)	019 (12)	178 (4)	332 (15)	2 (2)
H($W4a$)	1001 (12)	141 (4)	817 (16)	5 (2)

H($W2b$), H($W3b$) and H($W4b$) were not located.

The refinement with two isotropic half-oxygen atoms for O($W2$) and O($W4$) gave the following coordinates ($\times 10^3$)

	x	y	z
$W2X$	810	026	695
$W2Y$	791	020	789
$W4X$	943	143	822
$W4Y$	954	135	904

Then a full-matrix least-squares refinement of the data was attempted first with the anisotropic parameters for the water molecules and then with two half oxygen atoms with isotropic temperature factors for each O($W2$) and O($W4$) (designated $W2X$, $W2Y$, $W4X$, $W4Y$ in Table 1). These split atoms did not merge on full-matrix least-squares refinement. A refinement of occupancy of these positions with low order data indicated 50% occupancy in each site. The final distances are $W2X$–$W2Y$=0·62 Å, $W4X$–$W4Y$= 0·56 Å. There was no evidence, from the observed structure factors, that loss of O($W2$) and O($W4$) was occurring as a function of the length of time the crystal was exposed to the X-ray beam.

The disorder of oxygen atoms also implies disorder of the hydrogen atoms and this seems to be the case. The last three hydrogen atoms, one attached to each of the three most anisotropic water molecules, were not revealed in a final difference map which showed only a few low peaks (up to 0·3 e.Å^{-3}) around the calcium ion but none near the disordered water molecules. Therefore these hydrogen atoms, H($W2b$), H($W3b$), and H($W4b$) must be disordered.

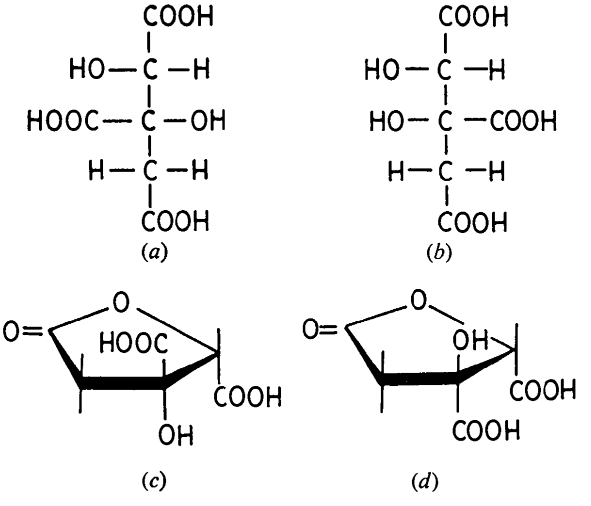


Fig. 1. Absolute configuration of (+)-*allo*-hydroxycitric acid. Fischer formulae are shown for (*a*) (+)-*allo*-hydroxycitric acid (*b*) (−)-hydroxycitric acid and diagrammatic formulae for (*c*) hibiscus acid (this work) (*d*) garcinia acid.

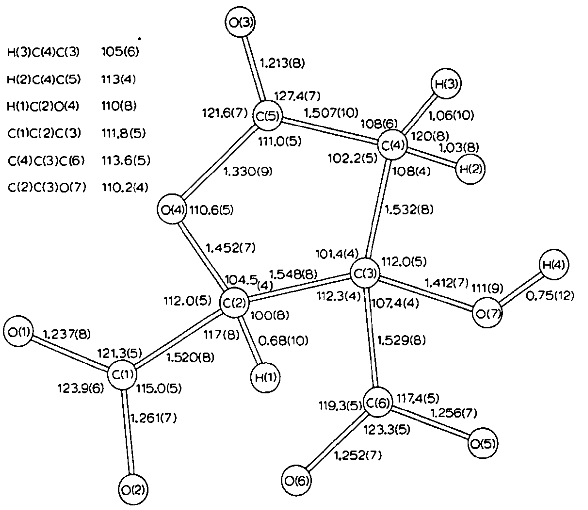


Fig. 2. Distances and angles in the lactone ion. Estimated standard deviations, in parentheses, are listed beside each value with respect to the last digit given.

The final R value was 0·056. The coordinates derived are listed in Table 1 and the structure factors are given in Table 2.

Computations

All initial calculations were calculated with an IBM 1620 computer with 20K memory. In earlier contributions from this laboratory a listing of programs is given (Johnson, 1965; Glusker, van der Helm, Love, Minkin & Patterson, 1968). The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962), the curve for Ca^{++} being used for the calcium ion. Scattering factors for hydrogen were the values given by Stewart, Davidson & Simpson (1965).

In the block-diagonal least-squares calculation, written by D. van der Helm for IBM 1620, weights were assigned as $1/[\sigma(F)]^2$, where $\sigma(F)$ was determined from counting statistics and measured instrumental uncertainties. The program omits reflections for which both $|F_o|$ and $|F_c|$ are small, and near-in reflections with large negative values of $|F_o|-|F_c|$. The quantity minimized is $\sum\omega(|kF_o|-|F_c|)^2$.

In the final stages of the calculation, when the disorder of the water molecules was being studied, calculations were done on a UNIVAC 1108 computer *via* a DCT 2000 terminal. A modified version of the full-matrix least-squares program of Gantzel, Sparks, Long & Trueblood (1969), which also minimizes $\sum\omega(|kF_o|-|F_c|)^2$, was used. Other calculations were done with the XRAY 70 system (Stewart, 1970).

Table 2. *Observed and calculated structure factors*

Each entry lists, in order, k, $|F_o|$, $|F_c|$ and α (phase angle in multiples of $2\pi \times 10^3$ radians). Unobserved reflections are denoted by an asterisk. Values of $|F_o|$ have been corrected for absorption, extinction and anomalous dispersion (Patterson, 1963, formula 5 with $\Delta f' = 0{\cdot}3$, $\Delta f'' = 1{\cdot}4$).

k	$\lvert F_o\rvert$	$\lvert F_c\rvert$	α
0,K,0			
2	642	-626	500
4	24	-20	500
6	501	518	0
8	293	-291	500
10	596	608	0
12	863	-883	500
14	347	-356	500
16	347	352	0
18	248	-251	500
20	232	239	0
22	96	-92	500
24	20	7	0
26	48	48	0
1,K,0			
1	219	159	750
2	928	-1009	750
3	652	638	250
4	83	-82	750
5	189	148	750
6	118	100	750
7	131	-144	750
8	691	695	250
9	499	-450	750
10	476	487	750
11	221	207	750
12	377	-353	750
13	280	294	250
14	216	216	250
15	361	-340	750
16	21	-13	750
17	406	390	250
18	69	-67	750
19	58	45	750
20	98	-111	750
21	83	74	250
22	15*	-19	750
23	152	154	250
24	24	32	250
25	148	-144	750
26	52	55	250
2,K,0			
0	226	232	0
1	117	120	0
2	548	566	0
3	35	14	0
4	849	-838	500
5	178	186	0
6	127	135	0
7	525	510	0
8	365	362	0
9	233	220	0
10	489	-487	500
11	159	-157	500
12	107	-112	500
13	232	225	0
14	32	50	0
15	155	167	0
16	188	-189	500
17	31	-31	500
18	379	380	0
19	186	193	0
20	280	-281	500
21	25	-31	500
22	250	257	0
23	50	43	0
24	33	15	0
25	47	-41	500
26	43	-44	500
3,K,0			
1	573	579	250
2	319	-297	250
3	813	797	250
4	28	-6	750
5	612	578	250
6	465	-467	750
7	569	-562	750
8	59	58	750
9	101	93	250
10	262	-264	750
11	70	65	750
12	30	20	250
13	302	-309	750
14	81	-69	750
15	79	60	250
16	51	56	750
17	218	-196	750
18	46	-45	250
19	299	305	250
20	44	-42	250
21	30	-40	750
22	77	68	250
23	78	-70	750
24	27	-36	250
25	100	94	250
4,K,0			
0	415	391	0
1	525	531	0
2	1047	-1065	500
3	118	113	0
4	522	529	0
5	140	-137	500
6	190	181	0
7	94	-95	500
8	276	-287	500
9	43	-37	500
10	374	366	0
11	119	113	0
12	201	-186	500
13	64	50	0
14	227	229	0
15	29	13	0
16	74	77	0
17	135	-147	500
18	369	-377	500
19	73	83	0
20	199	196	0
21	34	37	0
22	194	-198	500
23	27	-25	500
24	48	45	0
25	7*	-3	500
5,K,0			
1	124	125	250
2	205	213	250
3	496	511	250
4	237	237	250
5	519	-517	750
6	137	126	750
7	54	35	250
8	148	-148	250
9	293	297	250
10	91	92	250
11	165	-172	750
12	199	217	250
13	56	-32	250
14	76	75	250
15	466	-478	750
16	48	55	750
17	230	223	250
18	196	-214	250
19	33	-30	250
20	13*	6	250
21	98	-116	750
22	53	54	250
23	110	102	250
6,K,0			
0	903	-937	500
1	64	64	0
2	296	300	0
3	351	366	0
4	211	-198	500
5	49	-43	500
6	239	-234	500
7	337	-312	500
8	332	332	0
9	352	380	0
10	214	-203	500
11	128	130	0
12	204	193	0
13	61	67	0
14	89	99	0
15	42	46	0
16	225	-239	500
17	227	-220	500
18	204	210	0
19	159	166	0
20	272	-276	500
21	98	-103	500
22	69	63	0
7,K,0			
1	113	-125	750
2	66	-84	750
3	189	-187	750
4	23	4	750
5	51	-40	250
6	152	156	250
7	213	-204	750
8	66	-71	750
9	328	316	250
10	54	-59	250
11	16*	-10	750
12	90	101	250
13	145	-131	750
14	100	-104	750
15	137	125	250
16	123	117	250
17	146	-135	750
18	126	-123	750
19	139	143	250
20	8*	-16	750
8,K,0			
0	190	189	0
1	166	183	0
2	276	-302	500
3	186	-172	500
4	116	113	0
5	17*	4	0
6	59	-70	500
7	15*	22	0
8	200	-204	500
9	82	-81	500
10	237	238	0
11	100	99	0
12	90	-80	500
13	193	-199	500
14	42	25	0
15	30	-21	500
16	199	204	0
17	26	-23	500
18	77	-77	500
9,K,0			
1	168	-162	750
2	78	-80	750
3	68	49	250
4	113	115	250
5	29	-4	750
6	41	-40	750
7	49	38	250
8	13*	-20	750
9	81	-90	750
10	80	75	250
11	51	-49	750
12	11*	-27	250
13	174	180	250
14	63	65	250
10,K,0			
1	156	-153	500
2	308	300	0
3	33	-37	500
4	67	69	0
5	44	45	0
6	44	-43	500
7	75	-30	500
8	69	69	0
9	46	41	0
0,K,1			
1	565	550	250
2	270	293	0
3	549	-551	750
4	150	164	0
5	38	-41	750
6	328	-318	500
7	211	177	250
8	298	272	0
9	612	-576	750
10	382	362	0
11	253	234	250
12	65	82	0
13	598	-593	750
14	25	-19	500
15	117	95	250
16	179	188	0
17	174	169	250
18	345	338	0
19	56	-22	750
20	136	136	0
21	183	170	250
22	98	-107	500
23	67	-58	750
24	48	49	0
25	50	54	250
26	99	-103	500
1,K,1			
0	547	595	250
1	558	539	117
2	342	351	121
3	113	111	981
4	339	-344	932
5	506	-555	172
6	255	255	28
7	543	526	133
8	278	-291	71
9	889	897	757
10	233	263	933
11	245	-258	779
12	236	225	978
13	251	-236	12
14	298	-286	48
15	53	50	765
16	292	271	77
17	142	-166	946
18	383	-360	839
19	84	-83	46
20	119	-129	240
21	203	198	92
22	94	90	17
23	110	-112	841
24	237	-232	917
25	67	87	866
26	169	167	14
2,K,1			
0	66	63	250
1	1080	-1052	93
2	292	-331	763
3	257	-252	952
4	87	81	104
5	219	-229	877
6	337	-316	988
7	636	635	776
8	398	-386	953
9	550	-562	752
10	349	317	23
11	487	483	755
12	238	-225	40
13	117	128	38
14	208	228	766
15	157	144	210
16	123	123	756
17	230	227	768
18	48	-31	961
19	322	-343	787
20	99	88	43
21	257	-246	151
22	52	52	771
23	107	107	179
24	99	-91	858
25	115	105	101
26	73	78	130
3,K,1			
0	115	-115	250
1	297	307	116
2	325	-310	958
3	133	-140	112
4	847	873	28
5	137	-148	775
6	680	-664	13
7	226	234	824
8	376	375	9
9	195	-185	825
10	322	305	126
11	135	-127	250
12	76	-84	875
13	467	-449	810
14	372	358	940
15	150	147	38
15	332	-330	97
17	50	-47	905
18	71	66	156
19	218	-238	804
20	29	-30	990
21	64	73	74
22	143	-153	96
23	92	-88	899
24	93	91	961
25	47	47	58
4,K,1			
0	210	-206	750
1	486	-500	821
2	479	-437	760
3	345	342	837
4	181	179	24
5	60	55	66
6	82	-77	209
7	224	-221	767
8	70	-72	818
9	361	-364	224
10	117	-121	232
11	460	474	190
12	216	203	180
13	186	192	828
14	318	291	786
15	217	-233	924
16	147	-155	162
17	72	-69	884
18	155	-180	890
19	206	-200	241
20	22	-26	149
21	172	-176	846
23	97	-97	186
24	40	42	19
5,K,1			
0	509	-490	750
1	335	-325	806
2	275	279	850
3	76	-79	229
4	131	128	752
5	285	-290	160
6	301	303	880
7	306	323	186
8	109	-100	818
9	291	-283	155
10	39	42	984
11	348	342	225
12	213	206	66
13	163	166	824
14	163	-158	922
15	76	81	812
16	185	178	880
17	188	191	111
18	161	-157	989
19	79	-79	970
20	32	-33	947
21	30	-29	169
22	120	123	980
23	106	105	779
6,K,1			
0	32	-31	750
1	204	-194	169
2	89	82	249
3	233	225	157
4	100	-97	833
5	82	77	173
6	179	170	29
7	227	-229	137
8	212	218	755
9	389	-400	866
10	81	70	151
11	255	272	912
12	108	-112	868
13	204	199	197
14	124	-143	376
15	139	-154	5
16	41	-44	997
17	187	189	779
18	65	-61	32
19	165	173	158
20	81	-94	842
20	88	-94	842
21	167	174	827
22	89	-94	141
7,K,1			
0	78	-78	250
1	159	-157	986
2	224	-221	89
3	89	-72	915
4	333	317	990
5	112	106	18
6	294	-289	936
7	265	-283	199
8	220	227	977
9	209	-215	757
10	104	-128	988
11	99	103	887
12	156	-158	124
13	54	58	898
14	170	172	85
15	116	106	890
16	202	-207	923
17	89	-95	201
18	187	182	863
19	77	73	168
20	42	-43	150
8,K,1			
0	314	-312	750
1	368	354	237
2	175	162	179
3	156	162	965
4	104	-107	42
5	126	128	992
6	55	32	815
7	228	-229	758
8	82	75	84
9	231	-242	203
10	215	-203	137
11	260	265	240
12	178	171	240
13	91	86	877
14	123	-113	81
15	95	-88	247
16	45	-45	929
17	95	92	248
9,K,1			
0	91	84	250
1	187	-183	894
2	66	59	164
3	149	149	23
4	177	-177	42
5	71	-70	40
6	102	90	997
7	117	123	154
8	63	-64	859
9	148	-145	204
10	111	-108	159
11	123	119	230
12	69	73	929
13	132	138	936
14	154	-152	963
10,K,1			
0	42	48	750
1	117	114	760
2	103	107	814
3	105	113	188
4	41	-40	975
5	50	-42	963
6	94	89	99
7	101	107	897
8	62	-57	209
9	121	120	245
0,K,2			
0	607	-623	500
1	584	-590	750
2	418	-397	500
3	933	949	250
4	286	284	0
5	63	-52	250
6	38	-43	500
7	119	-125	750
8	530	-575	500
9	103	109	250
10	296	321	0
11	116	102	250
12	397	-377	500
13	64	42	750
14	320	305	0
15	52	-45	750
16	238	-278	500
17	295	-291	750
18	166	-164	500
19	203	199	250
20	165	156	0
21	16	-4	750
22	114	-110	500
23	103	-105	750
24	23	21	0
25	168	164	250
26	24	22	0
1,K,2			
0	390	387	0
1	391	-374	933
2	506	-506	45
3	473	477	245
4	441	450	991
5	831	-840	217
6	840	-698	238
7	556	525	246
8	514	-492	78
9	192	188	84
10	173	164	967
11	226	-203	102
12	153	-146	826
13	297	289	107
14	41	40	789
15	415	395	796
16	133	126	76
17	106	-84	848
18	319	-306	826
19	29	-21	17
20	155	158	93
21	188	181	767
22	112	-110	964
23	123	-122	781
24	12	-21	54
25	182	184	768
26	57	65	201
2,K,2			
0	144	152	0
1	326	356	853
2	104	110	967
3	904	889	150
4	330	343	51
5	449	461	834
6	346	-366	114
7	269	-277	923
8	287	292	944
9	99	108	868
10	326	-334	854
11	166	177	51
12	235	250	339
13	181	-187	809
14	171	-170	1
15	360	-342	160
16	172	-166	912
17	274	-284	904
18	42	23	959
19	89	-88	17
20	147	-147	42
21	48	-55	7
22	114	113	16
23	36	23	241
24	305	-122	101
25	58	-49	217
3,K,2			
0	929	-907	500
1	243	-252	775
2	508	489	923
3	747	731	819
4	99	91	75
5	305	-299	791
6	297	-311	946
7	427	416	753
8	149	155	192
9	251	234	161
10	255	-250	9
11	133	-131	922
12	227	210	18
13	233	297	807
14	79	87	842
15	119	-114	901
16	190	-188	938
17	208	-210	238
18	269	286	24
19	80	74	62
20	187	-179	25
21	73	-78	811
22	66	60	50
23	165	166	762
24	93	-98	176
25	116	112	237
4,K,2			
0	495	482	0
1	108	102	164
2	94	-92	116
3	172	174	407
4	85	-81	37
5	424	393	9
6	79	81	90
7	250	240	901
8	193	-202	70
9	92	92	904
10	333	335	12
11	208	202	97
12	346	-351	938
13	203	-192	192
14	168	169	886
15	164	157	234
16	117	-137	766
17	130	-130	1
18	36	-31	183
19	125	-125	942
20	129	129	952
21	27	-32	73
22	81	-87	822
23	89	-83	179
24	95	97	874
5,K,2			
0	38	27	0
1	227	214	857
2	256	-247	56
3	400	378	233
4	348	339	138
5	130	-111	223
6	223	-210	52
7	189	191	193
8	148	-132	800
9	254	-253	183
10	249	241	955
11	137	-132	249
12	154	-151	121
13	303	-312	799
14	19*	22	859
15	345	-331	174
16	175	-166	243
17	81	77	32
18	105	-116	231
19	16*	-29	870
20	114	111	911
21	86	87	779
6,K,2			
0	116	-121	500
1	135	-136	12
2	25	45	780
3	172	-181	30
4	77	92	83
5	155	154	925
6	106	112	238
7	170	148	155
8	173	170	73
9	178	-160	222
10	291	-293	92
11	150	-138	18
12	218	216	23
13	74	69	178
14	49	48	864
15	103	104	883
16	89	89	967
17	138	-139	818
18	121	120	79
19	117	126	760
20	133	-131	103
21	84	-84	982
7,K,2			
0	337	-324	500
1	222	-217	905
2	371	385	147
3	137	-131	227
4	50	20	926
5	458	471	239
6	153	-148	888
7	277	-273	221
8	243	239	982
9	51	44	924
10	100	-100	882
11	97	-100	850
12	145	158	195
13	74	-73	194
14	68	-70	239
15	95	89	236
16	147	-174	35
17	151	151	760
18	199	203	927
19	31	-32	853
8,K,2			
0	42	-43	500
1	67	59	989
2	108	-110	931
3	227	-215	154
4	82	77	932
5	139	141	228
6	140	147	81
7	41	32	887
8	145	-152	993
9	91	-88	975
10	121	120	887
11	79	79	19
12	81	-75	915
13	60	-53	193
14	168	189	913
15	197	199	117
16	49	-45	754
9,K,2			
0	214	216	0
1	89	82	836
2	157	-148	989
3	189	-187	849
4	150	140	98
5	160	152	775
6	98	100	816
7	118	102	218
8	163	-160	908
9	74	-76	986
10	125	119	12
11	122	139	933
12	38	-41	79
13	186	-183	785
10,K,2			
0	86	-88	500
1	47	-50	833
2	52	51	800
3	32	-31	195
4	118	-115	949
5	59	-62	156
6	150	-149	157
7	126	-129	832
0,K,3			
1	232	-225	250
2	250	-242	500
3	684	-693	750
4	707	740	0
5	84	-82	250
6	166	-155	500
7	24	18	250
8	36	31	0
9	232	-230	750
10	51	35	0
11	51	-29	250
12	394	-413	500
13	15*	46	250
14	386	405	0
15	206	221	250
16	473	-454	500
17	125	120	250
18	94	-99	500
19	100	-89	750
20	56	51	0
21	158	161	250
22	92	-92	500
23	62	-55	750
24	216	218	0
1,K,3			
0	196	-185	750
1	544	562	196
2	436	420	981
3	244	-240	239
4	341	-335	909
5	292	-273	827
6	537	532	929
7	260	258	228
8	105	-95	169
9	153	-165	90
10	224	-220	953
11	206	196	196
12	353	347	79
13	314	-271	135
14	263	-245	4
15	227	-209	36
16	278	251	795
17	217	201	124
18	179	-168	881
19	187	-176	219
20	71	-64	69
21	150	-154	857
22	89	94	966
23	109	102	758
24	121	-130	161
2,K,3			
0	189	196	250
1	171	165	811
2	199	197	2
3	310	306	989
4	324	-313	34
5	223	-250	193
6	531	546	982
7	132	156	143
8	217	-215	123
9	103	-111	240
10	30	34	67
11	121	136	844
12	142	131	964
13	42	43	393
14	175	-181	78
15	193	-187	962
16	190	187	982
17	33	34	983
18	191	-200	53
19	197	192	186
20	88	84	203
21	123	123	790
22	52	54	107
23	108	106	212
24	107	-110	169
3,K,3			
0	142	-151	750
1	105	-112	156
2	141	146	818
3	227	239	186
4	365	381	90
5	39	14	184
6	41	-37	71
7	116	-127	784
8	221	215	955
9	100	-90	781
10	78	-84	38
11	187	200	859
12	64	-57	109
13	71	-72	211
14	189	184	91
15	108	-113	120
16	341	-355	36
17	150	-145	399
18	50	44	143
19	104	91	138
20	66	-67	37
21	184	191	766
22	66	-57	943
23	128	-133	791
24	78	88	111
4,K,3			
0	136	-127	250
1	385	-410	780
2	332	-345	947
3	133	137	868
4	185	183	891
5	70	-79	771
6	281	-297	2
7	42	30	227
8	143	144	66
9	46	-93	95
10	49	122	917
11	98	96	166
12	283	-296	70
13	145	-147	208
14	334	313	952
15	135	132	797
16	128	-124	994
17	73	83	104
18	207	188	898
19	77	76	892
20	10*	21	79
21	50	-55	774
22	161	-173	971
5,K,3			
0	25	12	250
1	402	-422	802
2	287	294	54
3	295	312	854
4	276	-254	917
5	131	-134	789
6	167	153	62
7	162	138	124
8	94	-83	798
9	257	242	762
10	88	-64	227
11	198	-207	762
12	250	240	994
13	151	154	941
14	242	-249	988
15	69	-60	775
16	89	76	948
17	50	-44	869
18	64	-54	928
19	232	-224	249
20	73	-76	148
21	153	144	227
6,K,3			
0	99	100	250
1	114	-118	144
3	291	311	144
4	375	-378	38
5	184	-188	973
6	190	197	993
7	130	144	992
8	263	-247	871
9	105	-110	869
10	37	-33	891
11	35	-31	11
12	238	245	879
13	66	56	86
14	179	-160	969
15	63	-69	94
16	233	227	18
17	211	213	878
18	89	-103	192
7,K,3			
0	157	162	250
1	159	158	763
2	114	-117	129
3	114	-111	31
4	175	180	12
5	88	92	986
6	253	-255	7
7	27	19	861
8	133	135	905
9	74	54	227
10	159	157	100
12	89	-90	168
13	88	-80	797
14	148	152	58
15	227	248	94
16	76	-80	929
17	66	71	755
8,K,3			
0	56	-47	750
1	14*	15	245
2	76	-83	854
3	103	-89	103
4	183	168	949
5	103	-131	820
6	141	-130	961
7	80	-93	122
8	98	107	140
9	27	14	58
10	11*	19	790
11	109	119	109
12	114	-103	910
13	142	-130	28
14	112	117	994
15	76	77	172
9,K,3			
0	30	6	750
1	137	-125	250
2	45	45	133
3	196	-204	219
4	167	-157	91
5	93	-96	923
6	83	86	12
7	82	79	138
8	46	-46	872
9	76	-87	228
10	103	-96	107
0,K,4			
0	327	346	0
1	325	311	250
2	224	218	0
3	715	-629	750
4	112	126	0
5	199	167	250
6	189	-186	500
7	97	-131	750
8	171	174	0
9	52	59	250
10	132	129	0
11	229	227	250
12	179	-172	500
13	357	-377	750
14	197	-194	500
15	139	125	250
16	148	-154	500
17	48	-27	750
18	50	56	0
19	41	-53	750
20	109	116	0
21	93	85	250
22	100	-95	500
23	198	-181	750
1,K,4			
0	273	267	0
1	56	-45	962
2	133	-110	154
3	315	297	21
4	99	-137	176
5	39	-32	825
6	192	215	159
7	131	-136	907
8	152	-158	938
9	48	54	909
10	354	342	920
11	123	128	868
12	289	-304	69
13	52	45	942
14	219	214	919
15	219	-220	47
16	87	92	244
18	63	-67	842
19	56	-50	142
20	168	153	928
21	53	-42	819
22	146	-145	909
23	66	-68	849
2,K,4			
0	217	-209	500
1	137	-136	209
2	306	310	988
3	368	-368	782
4	36	-27	61
5	527	-543	243
6	149	-144	922
7	426	-441	756
8	169	174	145
9	231	235	813
10	183	-201	164
11	133	142	949
12	19*	-11	212
13	187	175	235
14	85	-80	971
15	312	298	786
16	163	-157	107
17	159	159	215
18	192	182	957
19	58	-52	102
20	89	-89	121
21	119	-108	236
22	19	-12	758
3,K,4			
0	39	-21	500
1	393	-394	871
2	122	109	16
3	78	80	821
4	69	66	803
5	149	149	214
6	111	-121	110
7	30	-35	859
8	317	309	956
9	71	78	108
10	293	-304	0
11	117	-127	92
12	216	219	23
13	207	219	796
14	34	-32	963
15	53	-46	811
16	59	-56	756
17	99	98	790
18	166	164	960
19	22	-12	882
20	166	-160	31
21	42	42	226
22	129	125	55
4,K,4			
0	71	68	0
1	170	171	35
2	289	-273	859
3	138	133	849
4	105	122	922
5	392	-394	763
6	66	50	115
7	214	-223	214
8	158	155	972
9	27	-29	192
10	58	58	854
11	230	227	92
12	121	115	245
13	132	-134	239
14	76	87	798
15	216	-202	780
16	116	109	965
17	169	149	767
18	62	-68	168
19	58	-58	943
20	61	-51	233
21	133	134	223
5,K,4			
0	123	101	0
1	242	-285	795
2	178	-181	3
3	46	-150	186
4	159	157	21
5	85	91	769
6	193	193	937
7	81	77	124
8	279	-287	1
9	41	-51	829
10	180	172	72
11	43	43	772
12	146	-127	901
13	116	130	756
14	200	201	80
15	83	93	958
16	55	-64	6
17	110	103	119
18	54	-40	77
19	76	-68	130
6,K,4			
0	103	-116	500
1	166	188	913
2	42	-51	833
3	337	347	175
4	177	-190	848
5	266	-277	249
6	235	255	762
7	227	-220	752
8	85	93	235
9	67	64	787
10	46	-50	823
11	83	106	914
12	57	73	28
13	193	-181	765
14	34	45	41
15	148	-149	139
16	48	59	843
17	122	117	243
7,K,4			
0	139	-127	500
1	105	103	250
2	67	-31	938
3	207	178	800
4	63	49	87
5	77	-82	994
6	105	-87	925
7	42	-33	154
8	84	54	98
9	80	77	64
10	183	-167	4
11	68	-70	32
12	211	202	16
13	110	106	847
14	75	-69	973
15	119	-124	788
8,K,4			
0	76	71	0
1	142	124	130
2	132	-155	961
3	217	-206	230
4	106	-101	218
5	224	-208	762
6	65	78	136
7	164	149	800
8	11*	-4	816
9	82	-83	817
10	80	71	959
11	61	61	217
9,K,4			
0	139	130	0
1	164	150	917
2	111	-109	932
3	61	-59	984
4	66	-73	758
5	70	-60	46
0,K,5			
1	69	72	250
2	149	-119	500
3	16*	1	250
4	157	142	0
5	301	-301	750
6	302	-270	500
7	78	84	250
8	95	77	0
9	115	-119	750
10	147	141	0
11	96	112	250
13	186	-180	750
14	214	228	0
15	88	-107	750
16	131	-138	500
17	127	141	250
18	107	97	0
19	28	-15	750
20	27	39	0
21	65	-71	750
1,K,5			
0	125	138	250
1	270	269	213
2	53	34	44
4	79	80	44
5	38	30	858
6	68	-70	133
7	91	-94	980
8	119	123	238
9	231	-239	228
10	103	130	995
11	313	-317	751
12	161	-176	172
13	121	127	816
14	46	53	201
15	346	-142	950
16	62	-65	230
17	64	-61	823
18	63	58	27
19	185	191	839
20	25	16	973
2,K,5			
0	310	296	250
1	132	-146	905
2	308	318	50
3	54	-56	239
4	328	-336	2
5	44	52	27
6	255	250	26
7	134	130	786
8	227	-235	980
9	187	-163	942
10	78	89	926
11	43	45	798
12	211	211	887
13	81	85	930
14	192	-193	0
15	85	105	929
16	172	155	77
17	81	81	184
18	82	-84	13
19	116	-109	59
20	25	30	983
3,K,5			
0	261	267	250
1	261	-248	218
2	184	206	931
3	202	198	208
4	51	-53	99
5	27	-26	790
6	80	75	941
7	346	350	760
8	43	25	948
9	270	270	238
10	128	121	167
11	111	-94	163
12	146	158	890
13	95	140	226
14	112	-121	986
16	118	95	8
17	190	175	764
18	24	30	158
19	171	-167	772
4,K,5			
0	237	251	250
1	72	-68	96
2	36	45	234
3	95	-85	830
4	225	214	9
5	60	56	970
6	165	-160	970
7	102	101	249
8	84	80	997
9	125	-121	189
10	35	29	72
11	55	72	162
12	112	-117	92
13	11*	4	943
14	115	124	973
15	122	128	50
16	201	-211	10
17	63	-62	987
18	93	105	970
5,K,5			
0	18*	12	750
1	250	-268	801
2	51	40	857
3	180	-179	134
4	51	50	839
5	37	-38	776
6	47	54	957
7	117	109	234
8	11*	-14	944
9	180	184	773
10	59	66	898
11	216	228	232
12	62	62	223
13	140	-150	230
14	68	77	985
15	35	39	66
6,K,5			
0	61	60	250
1	60	-63	22
2	101	101	885
3	101	100	18
4	188	-189	988
5	174	-173	907
6	217	238	42
7	128	132	936
8	104	-115	102
9	99	-107	787
10	35	33	240
11	30	-29	216
12	33	36	109
13	67	74	123
14	173	-170	26
7,K,5			
0	38	-38	750
1	100	-108	142
2	98	-101	236
3	85	-91	816
4	137	-137	879
5	60	-44	801
6	102	97	100
7	81	-75	195
8	91	-85	238
9	150	-143	752
10	75	-72	911
11	161	134	754
8,K,5			
0	49	-44	750
1	14	22	5
2	242	-237	58
3	65	-64	787
4	154	145	999
5	60	73	905
6	123	-133	977
0,K,6			
0	51	-56	500
1	183	160	250
2	91	88	0
3	47	-57	750
4	16*	-19	500
5	297	210	250
6	67	61	0
7	150	-129	750
8	15*	1	0
9	76	-85	750
10	124	-117	500
11	113	88	250
12	123	118	0
14	104	-123	500
15	201	200	250
16	26	-8	500
17	151	-138	750
1,K,6			
0	241	233	0
1	71	68	201
2	372	-359	988
4	212	191	905
5	113	-110	756
6	111	92	911
7	117	130	891
8	212	-202	82
9	30	-24	947
10	172	171	13
11	85	-78	777
12	118	-114	54
13	99	97	824
14	42	39	4
15	36	-28	765
16	82	96	90
17	76	91	909
2,K,6			
0	37	35	0
1	86	95	55
2	76	78	219
3	137	130	193
4	117	124	219
5	164	162	776
6	75	83	855
7	190	201	149
8	99	-83	1
9	81	-86	189
10	43	42	64
11	21	23	918
12	63	-54	753
13	94	96	133
14	41	-45	870
15	134	-135	197
16	66	-60	186
17	107	-121	795
3,K,6			
0	370	-361	500
1	21*	-23	918
2	102	105	93
3	133	122	113
4	121	-132	81
5	88	-85	105
6	16*	6	41
7	60	-61	888
8	118	124	9
9	80	73	905
10	157	-150	978
11	21	-23	774
12	81	87	974
13	49	49	3
14	48	60	920
15	81	-45	194
16	51	-83	16
4,K,6			
0	147	-144	500
1	26	23	72
2	118	106	934
3	162	167	793
4	45	56	246
5	64	62	197
6	69	-66	919
7	97	105	940
8	56	51	31
9	81	81	197
10	81	-80	55
11	51	-46	776
12	95	105	95
13	140	143	797
14	36	-35	796
5,K,6			
0	425	394	0
1	46	40	125
2	317	-294	952
3	58	-48	19
4	36	33	828
5	90	-93	836
6	68	75	178
7	48	47	799
8	104	-98	990
9	33	-27	965
10	176	178	30
11	24	24	996
12	168	-187	966
6,K,6			
0	47	-28	500
1	150	-150	246
2	154	-171	212
3	118	-110	762
4	87	85	211
5	120	-121	248
6	25	20	844
7	110	112	208
8	75	-80	851
9	53	72	759
7,K,6			
0	38	-27	500
1	140	-152	31
2	152	155	982
0,K,7			
1	212	-175	750
2	91	76	0
3	18*	17	250
4	95	71	0
5	80	-47	250
6	135	-105	500
7	87	-90	750
8	77	57	0
9	78	74	250
10	55	61	0
11	202	-209	750
12	10*	38	0
13	142	145	250
1,K,7			
0	166	166	250
1	128	119	213
2	89	-84	107
4	160	134	948
5	25	-23	984
6	117	-97	931
7	173	155	238
8	48	46	68
9	198	175	831
10	73	68	239
11	160	-154	855
12	19	-38	174
2,K,7			
0	64	-51	750
1	33	44	72
2	143	129	8
3	77	-70	178
4	185	-147	998
5	84	-90	102
7	135	135	216
8	117	-101	945
9	177	167	755
10	42	53	42
11	81	-94	842
3,K,7			
0	43	47	250
1	180	158	804
2	61	61	878
3	50	-48	791
4	73	-62	829
5	87	-76	766
6	119	110	28
7	56	-54	192
8	106	-109	95
9	120	132	233
10	68	77	14
4,K,7			
0	80	-56	250
1	137	131	771
2	90	-131	45
3	78	-96	915
4	92	97	28
5	37	30	102
6	53	-53	39
7	101	108	761
8	69	69	553
5,K,7			
0	111	-95	750
1	106	100	199
2	29	26	248

Discussion of the structure

In the lactone of (+)-*allo*-hydroxycitric acid the two carboxyl groups are on opposite sides of the lactone ring and the absolute configuration of the acid is shown in Fig. 1. The result for the lactone of (−)-hydroxycitric acid (garcinia acid) (Glusker, Minkin, & Casciato, 1971) is also shown.

In Fig. 2 the distances and angles in the lactone ion are given. The four C–O distances in the carboxyl groups are similar (1·237, 1·261, 1·256, 1·252 Å) indicating that both carboxyl groups are ionized. The planarities of various groupings in the lactone ion are shown in Table 3.

Table 3. *Planarities of various groups in the lactone ion*

Deviations (Å) from the least-squares plane through atoms marked with an asterisk are shown.

(*a*) Carboxyl groups and nearby oxygen atoms

O(1)	−0·0001*	O(5)	0·0032*
O(2)	−0·0001*	O(6)	0·0033*
C(1)	0·0003*	C(6)	−0·0089*
C(2)	−0·0001*	C(3)	0·0024*
O(4)	0·0020	O(7)	−0·2144

(*b*) Lactone ring

	O–CO–C	–C–O–CO–C	C–O–C	Whole ring
C(2)	0·0071	0·0000*	0·0022*	0·1250*
C(3)	0·5111	0·4850	0·5074	0·2399*
C(4)	−0·0025*	−0·0303	−0·0034*	−0·2050*
C(5)	0·0086*	0·0000*	0·0082*	−0·0100*
O(3)	−0·0034*	−0·0067	−0·0017*	0·0852*
O(4)	−0·0027*	0·0000*	−0·0053*	0·0149*

The coordination around the calcium ion is listed in Table 4. The calcium ion is surrounded by nine oxygen atoms and the coordination polyhedron resembles a square antiprism (which is the situation in the salt of garcinia acid with only eight oxygen atoms in the coordination polyhedron) but with an additional square pyramid on one side. This is illustrated in Fig. 3. The average Ca···O distance of 2·518 Å is longer than that for the garcinia salt (2·456 Å).

Table 4. *Coordination around the calcium ion*

Ca–O(5^{i})	2·411 (4) Å
Ca–O(7^{i})	2·449 (5)
Ca–O($W4^{i}$)	2·475 (8)
Ca–O($W1^{iii}$)	2·481 (5)
Ca–O(6^{ii})	2·503 (4)
Ca–O($W3$)	2·506 (7)
Ca–O(5^{ii})	2·595 (4)
Ca–O(1)	2·618 (5)
Ca–O(2)	2·635 (5)

i	x,	y,	$z-1$
ii	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$1-z$
iii	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$-z$
iv	$1+x$,	y,	z
v	$1\frac{1}{2}-x$,	$-y$,	$\frac{1}{2}+z$
vi	$x-\frac{1}{2}$,	$\frac{1}{2}-y$,	$1-z$
vii	$1\frac{1}{2}-x$,	$-y$,	$z-\frac{1}{2}$

The hydrogen bond system is shown in Table 5. The fact that three hydrogen atom positions are undetermined probably indicates disorder, either because they are involved in hydrogen bonds to markedly anisotropic oxygen atoms or each to two different oxygen atoms. These possibilities are listed in Table 5. There are nine hydrogen bonds, as for garcinia, with an average distance of approximately 2·82 Å.

A comparison of the surroundings of a lactone ion in the two salts is given in Table 6. It is seen that the surroundings are very similar, especially for O(2), O(5), and O(7) which are probably the most negatively charged oxygen atoms, particularly the first two. In three cases in this structure calcium coordination re-

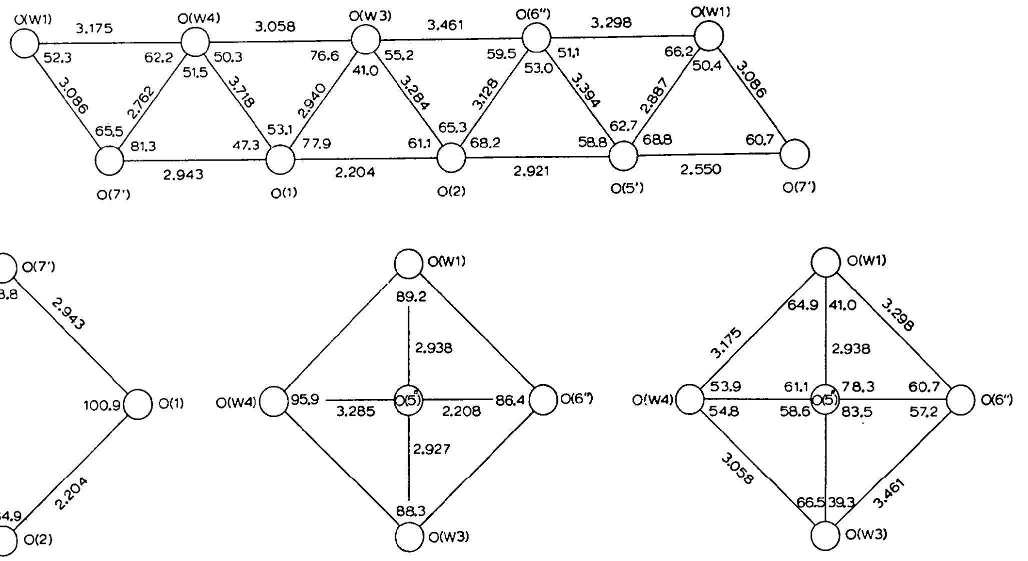


Fig. 3. Coordination around the calcium ion. Distances and angles involving the oxygen atoms of the coordination sphere (a square antiprism with a pyramid, apex O(5''), on one square side) are shown. Estimated standard deviations are 0·003–0·008 Å for distances and 0·1–0·3° for angles.

Table 5. *Hydrogen bonds*

D-H···*A*	*D*-H e.s.d. 0·1 Å	H···*A* e.s.d. 0·1 Å	*D*···*A* e.s.d. 0·007 Å	∠*A*···H-*D* e.s.d. 10°	∠H-*D*···*A* e.s.d. 10°
O(7)—H(4)··· .O(*W*2)	0·75	1·90	2·633	166	10
O(*W*1)-H(*W*1*a*)···O(2^{vi})	0·56	2·33	2·877	166	12
O(*W*1)-H(*W*1*b*)···O(2)	0·88	2·07	2·844	146	24
O(*W*2)-H(*W*2*a*)···O(1^{v})	0·70	2·11	2·738	149	23
O(*W*3)-H(*W*3*a*)···O(*W*1^{iv})	0·70	2·37	3·015	155	19
O(*W*4)-H(*W*4*a*)···O(6^{iv})	0·53	2·27	2·726	146	28

In the headings *D* = donor and *A* = acceptor

Two possible schemes in terms of *W*2*X*, *W*2*Y*, *W*4*X*, *W*4*Y* are given below. Both of these schemes may occur in the crystal explaining the disorder.

		O···O Distance
(*a*)	O(*W*3)-H(*W*3*b*)···*W*4*X*	2·730 Å
	*W*4*X*—H(*W*4*b*)···O(3^{v})	2·915
	*W*2*X*—H(*W*2*b*)···*W*4*X*	2·989

		O···O Distance
(*b*)	O(*W*3)-H(*W*3*b*)···O(3^{vii})	3·047 Å
	W(4*Y*)-H(*W*4*b*)···*W*2*X*	2·834
	*W*2*X*—H(*W*2*b*)···*W*2$Y^{v \text{ or } vii}$	2·643

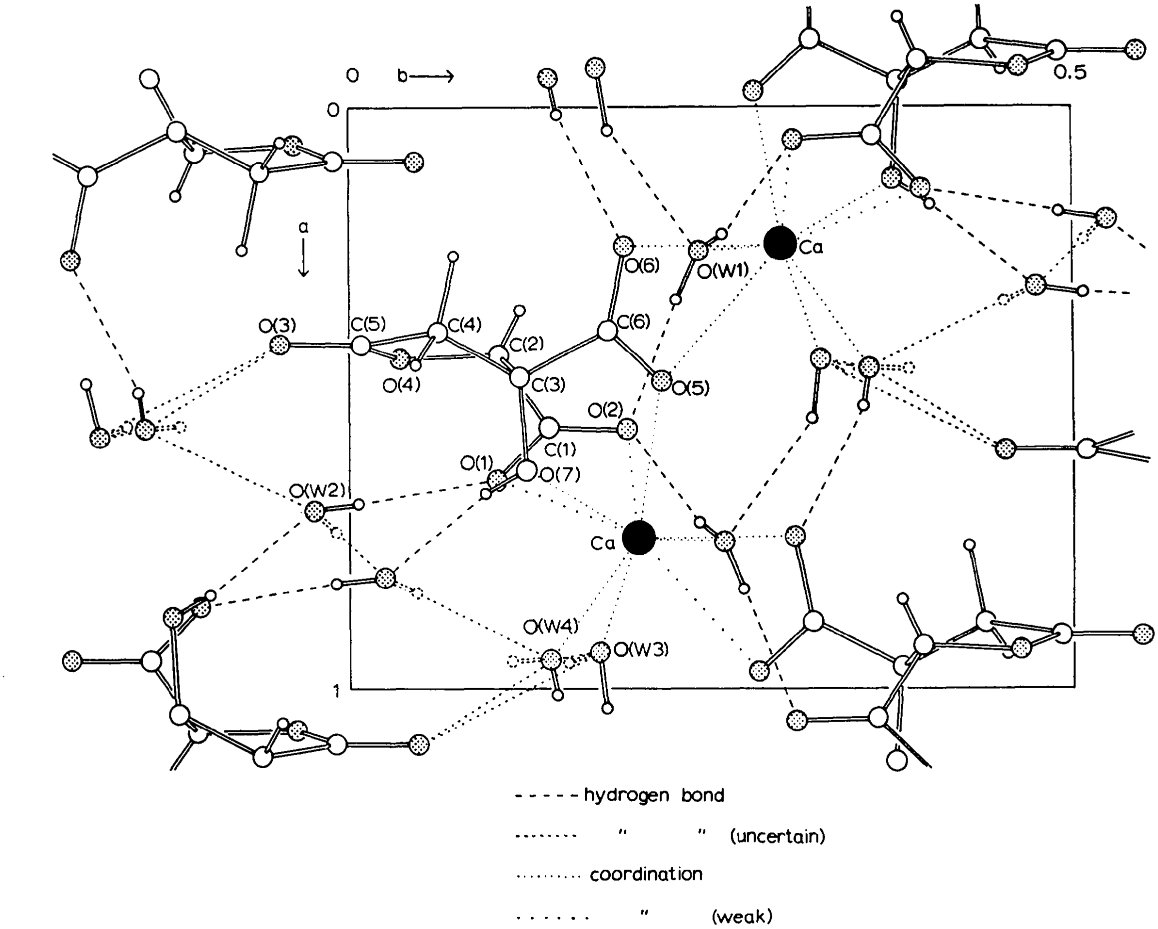
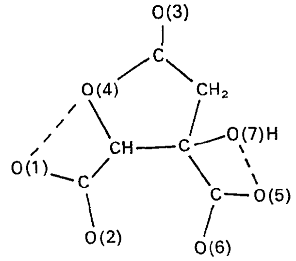


Fig. 4. General packing in the unit cell. View down the *c* axis. Calcium ions are black and oxygen atoms are stippled. Uncertain hydrogen atoms are marked with broken lines. Their positions are only indicated because to omit them might confuse the reader on the identities of water molecules. The channels of O(*W*2) and of O(*W*3) with O(*W*4) water molecules can be seen.

places hydrogen bonding in the garcinia salt and in one case hydrogen bonding replaces calcium coordination. The general packing in the unit cell is illustrated in Fig. 4. Crystals of this salt are slightly less dense than those of the garcinia salt, presumably owing to looser packing, and these crystals are less stable. The channels of water molecules [O(*W*2) in one area and O(*W*3) and O(*W*4) in another] parallel to the *c* axis can be seen clearly in Fig. 4. Water, especially O(*W*2) which is loosely held, is probably easily lost from these channels, possibly explaining the efflorescence of the crystals.

Table 6. *Comparison of the surroundings of the lactone ion*



	Hibiscus	Garcinia
O(1)	H bond from O(*W*2) Ca coordination	H bond from O(*W*3) H bond from O(7)
O(2)	H bond from O(*W*1) H bond from O(*W*1′) Ca coordination	H bond from O(*W*1) H bond from O(*W*1′) H bond to O(*W*4)
O(3)	H bond from O(*W*3) or O(*W*4)	Ca coordination
O(4)	Nothing	Nothing
O(5)	Ca coordination Ca′ coordination	Ca coordination Ca′ coordination
O(6)	Ca coordination	H bond from O(*W*2)
O(7)	H bond to O(*W*2) Ca coordination	H bond to O(1) Ca coordination

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References

Boll, P., Sørensen, E. & Balieu, E. (1969). *Acta Chem. Scand.* **23**, 286.

Cahn, R. S., Ingold, C. & Prelog, V. (1966). *Angew. Chem. Int. Ed.* **5**, 385.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891.

Gantzel, P. K., Sparks, R. A., Long, R. E. & Trueblood, K. N. (1969). *UCLALS4*. Program in Fortran IV.

Glusker, J. P., van der Helm, D., Love, W. E., Minkin, J. A. & Patterson, A. L. (1968). *Acta Cryst.* **B24**, 359.

Glusker, J. P., Minkin, J. A. & Casciato, C. A. (1971). *Acta Cryst.* **B27**, 1284.

Glusker, J. P., Minkin, J. A., Casciato, C. A. & Soule, F. B. (1969). *Arch. Biochem. Biophys.* **13**, 573.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–207. Birmingham: Kynoch Press.

Johnson, C. K. (1963). 1620 Programs from I.C.R. I.C.R. No. 10. Absorption Factors for a Crystal Ground as an Ellipsoid of Revolution.

Johnson, C. K. (1965). *Acta Cryst.* **18**, 1005.

Lewis, Y. S. & Neelakantan, S. (1965). *Phytochemistry*, **4**, 619.

Patterson, A. L. (1963). *Acta Cryst.* **16**, 1255.

Stewart, J. M. (1970). *The X-ray System of Crystallographic Programs for Any Computer having a Pidgin Fortran Compiler*. Version of July 1970.

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, A. C. A. Meeting, M.I.T., Cambridge, Mass., U.S.A. March 28–30.

Acta Cryst. (1972). **B28**, 2505

The Crystal Structure of Manganese Chlorophosphate, $Mn_2(PO_4)Cl$

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Manganese chlorophosphate, $Mn_2(PO_4)Cl$, crystallizes in the space group $Pna2_1$, with unit-cell dimensions $a = 11{\cdot}364$ (2), $b = 8{\cdot}0965$ (7), and $c = 4{\cdot}9053$ (4) Å ($Z = 4$). A three-dimensional structural analysis, using automatic diffractometer data, has been completed and refined by full-matrix least-squares procedures to a residual $R = 0{\cdot}030$ ($R_w = 0{\cdot}049$). The structural unit can be described as two distorted edge-sharing octahedra of anions about the two non-equivalent manganese atoms, which are further linked through edge sharing by phosphate tetrahedra.

Introduction

Many minerals having the stoichiometry $M_2(XO_4)Z$ (where M is a divalent metal or metals, X is P, As, or V, and Z is a halogen or hydroxyl group) are known (Richmond, 1940), but few crystal structures have been reported. Recently, several crystallographic structures for relevant phosphate materials have been published: triplite, $(Mn, Fe)_2(PO_4)F$, (Waldrop, 1969); triploidite, $(Mn, Fe)_2(PO_4)$ (OH), (Waldrop, 1970); wagnerite, $Mg_2(PO_4)F$, (Coda, Giuseppetti & Tadini, 1967); tar-

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† See footnote p. 2525.