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The Structure and Absolute Configuration of the Calcium Salt of Garcinia Acid, the Lactone of (–)-Hydroxycitric Acid

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The calcium salt of the lactone of (–)-hydroxycitric acid crystallizes in the orthorhombic system as a tetrahydrate. Unit-cell dimensions are $a=8{\cdot}680$, $b=17{\cdot}299$, $c=7{\cdot}135$ Å. The space group is $P2_12_12$ with four units of $\mathrm{Ca(C_6O_7H_4).4H_2O}$ per cell. 1371 independent data, of which 97 were below the threshold of measurement, were collected on a manual diffractometer with Cu $K\alpha$ radiation (to $2\theta=160°$). The structure was solved by heavy-atom techniques and was refined by the full-matrix least-squares method to an R value of 0·050. All hydrogen atoms were found from a difference map and their parameters were refined. The absolute configuration of the free (–)-hydroxycitric acid, determined from anomalous dispersion measurements on the lactone salt, is (1*S*:2*S*)-1,2-hydroxy-1,2,3-propanetricarboxylic acid. The two carboxyl groups are *cis* 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. The calcium ion is surrounded by eight oxygen atoms in a square antiprism arrangement, with Ca–O distances of 2·39–2·52 Å, and with one face of the coordination polyhedron shared with that of another calcium ion.

Crystals of the calcium salt of garcinia acid, the lactone of (–)-hydroxycitric acid, were provided by Dr Y. S. Lewis of the Central Food Technological Research Institute, Mysore, India; the acid had been isolated from the fruits of *Garcinia cambogia* Desr. (Lewis & Neelakantan, 1965). There are two asymmetric carbon atoms in hydroxycitric acid and hence four isomers exist. Therefore, an X-ray crystallographic study was undertaken to determine the absolute configuration of this isomer that is accumulated by plants. It is the enantiomorph of a hydroxycitrate which is a substrate of isocitric dehydrogenase in the Krebs cycle (Martius & Maué, 1941). It had also been found (Watson, Fang & Lowenstein, 1969) that garcinia acid inhibits citrate cleavage enzyme more powerfully than does (+)-*allo*-hydroxycitrate, another hydroxycitrate accumulated by plants. This crystallographic study was also made to determine the nature of the packing around the calcium ion and of the hydrogen bonding in the crystal.

Experimental

The crystals are orthorhombic with cell dimensions $a=8{\cdot}680\pm0{\cdot}004$, $b=17{\cdot}299\pm0{\cdot}015$, $c=7{\cdot}135\pm0{\cdot}005$ Å which were measured on the General Electric XRD-5 diffractometer with copper radiation [$\lambda(\mathrm{Cu}\ K\alpha_1)=1{\cdot}5405$ Å]. The space group is $P2_12_12$ (from the systematic absences $h00$, h odd and $0k0$, k odd) with $Z=4$. The observed density is 1·88 g.cm^{-3}, measured by flotation in a mixture of methylene iodide and carbon tetrachloride. The density calculated for four units of $\mathrm{Ca\ (C_6O_7H_4).4H_2O}$ is 1·86 g.cm^{-3}. The crystals became slightly damp on standing in air for long periods of time (a year or more), presumably due to a tendency to deliquescence.

Data were collected on a crystal of size $0{\cdot}28\times0{\cdot}28\times0{\cdot}13$ mm. Intensities were measured on a General Electric XRD-5 diffractometer with the θ–2θ scan technique and with nickel-filtered copper radiation. 1371 independent reflections were scanned to $2\theta=160°$, and of these 97 were below the threshold of measurement (judged from the diffractometer trace). The data were corrected for the Lorentz and polarization factors.

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Absorption corrections were applied ($\mu = 53{\cdot}1$ cm^{-1}) for an ellipsoid of revolution (a close approximation to the crystal shape).

Solution of the structure

The position of the calcium ion was determined from an $|F|^2$ map. The positions of the lactone ion and of two water molecules were found by vector superposition methods and the first trial structure gave an R value of 0·41. A Fourier synthesis was calculated which showed that one more water molecule was in a general position and that the other water molecules were in two special positions, 0, 0, z and $\frac{1}{2}$, 0, z'. The R value was then 0·29 and dropped to 0·099 after five cycles of isotropic least-squares and to 0·084 after anisotropic refinement.

Absolute configuration

The absolute configuration of the lactone ion was established by a measurement of Friedel-related pairs of reflections from integrated Weissenberg photographs taken with chromium radiation. A comparison of experimental values of the ratio $(I_+ - I_-)/(I_+ + I_-)$, where I_+ is the intensity of the reflection hkl and I_- is the intensity of the reflection $\bar{h}\bar{k}\bar{l}$) and computed values (Patterson, 1963) have already been listed (Glusker, Minkin, Casciato & Soule, 1969) for the 15 highest values of the measured ratio. In all measured cases, the sign of $(I_+ - I_-)$ indicates that the absolute configuration, in the Cahn—Ingold notation (Cahn, Ingold & Prelog, 1966), corresponds to (1*S*:2*S*)-1,2-hydroxy-1,2,3-propanetricarboxylic acid (or 2*S*:3*S*-2-hydroxycitric acid) for the free (−)-hydroxycitric acid. This had also been deduced from chemical studies. Lewis & Neelakantan (1965) established the configuration at one chiral center from Hudson's lactone rule. Boll, Sørensen & Balieu (1969) determined the absolute configuration from pK values, synthesis, nuclear magnetic resonance and infrared spectra, ORD and CD curves, and a calculation of partial molar rotations. The results from all methods were in agreement. The Fischer formulae for the free acid and the lactone are

Table 1. *Final parameters of atoms*

Positional parameters are expressed as fractions of cell edges.

Anisotropic temperature factors are expressed as:

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

Isotropic temperature factors are of the form $\exp(-B\sin^2\theta/\lambda^2)$, with B's 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	10^4b^{11}	10^4b^{22}	10^4b^{33}	10^4b^{12}	10^4b^{13}	10^4b^{23}
Ca	0·8141 (1)	0·0477 (1)	0·0704 (2)	59 (1)	11 (1)	76 (2)	5 (1)	−7 (3)	0 (1)
O(1)	0·2051 (5)	0·1959 (2)	0·7115 (7)	96 (6)	15 (1)	107 (9)	−19 (5)	−66 (13)	15 (6)
O(2)	0·0556 (5)	0·1084 (2)	0·5709 (7)	91 (5)	12 (1)	85 (7)	−14 (4)	−5 (13)	4 (6)
O(3)	0·2426 (6)	0·3749 (3)	0·2072 (7)	110 (6)	16 (1)	114 (10)	−39 (5)	−4 (13)	14 (6)
O(4)	0·1443 (5)	0·3011 (2)	0·4327 (7)	98 (6)	11 (1)	76 (8)	−20 (4)	−29 (12)	2 (6)
O(5)	0·0812 (5)	0·0774 (2)	0·1350 (6)	69 (5)	9 (1)	98 (8)	4 (4)	2 (11)	−25 (6)
O(6)	0·2718 (5)	0·1525 (3)	0·2390 (8)	60 (5)	22 (2)	159 (11)	5 (5)	7 (12)	−42 (7)
O(7)	−0·1318 (5)	0·1744 (2)	0·2195 (7)	55 (4)	11 (2)	105 (9)	0 (4)	−23 (11)	−19 (6)
O(*W*1)	0·7963 (5)	0·0270 (3)	0·4131 (7)	87 (6)	15 (1)	84 (8)	−3 (5)	−20 (12)	−6 (6)
O(*W*2)	0·5615 (9)	0·0892 (5)	0·1625 (16)	84 (8)	38 (3)	232 (20)	45 (7)	76 (20)	66 (14)
O(*W*3)	0·6627 (6)	−0·0480 (4)	0·8776 (7)	81 (6)	21 (2)	123 (10)	1 (5)	−31 (12)	−1 (7)
O(*W*4)	0·0000	0·0000	0·8306 (8)	78 (7)	10 (2)	60 (11)	−2 (6)	0	0
O(*W*5)	0·5000	0·0000	0·5655 (15)	92 (10)	60 (5)	144 (17)	−13 (11)	0	0
C(1)	0·1110 (6)	0·1751 (3)	0·5892 (8)	63 (6)	10 (1)	63 (9)	−8 (5)	14 (14)	1 (7)
C(2)	0·0444 (6)	0·2342 (3)	0·4513 (8)	64 (6)	10 (2)	59 (10)	−8 (5)	5 (13)	−24 (7)
C(3)	0·0199 (6)	0·2028 (3)	0·2495 (8)	60 (6)	7 (1)	51 (8)	−3 (5)	1 (13)	10 (6)
C(4)	0·0589 (8)	0·2738 (4)	0·1307 (9)	88 (8)	11 (2)	72 (10)	−5 (6)	2 (15)	4 (7)
C(5)	0·1585 (6)	0·3219 (3)	0·2508 (9)	68 (7)	10 (2)	93 (11)	−15 (5)	−9 (14)	13 (7)
C(6)	0·1346 (6)	0·1375 (3)	0·2055 (8)	63 (6)	12 (2)	51 (9)	6 (5)	−12 (13)	1 (7)

	x	y	z	B	attached to
H(1)	−0·190 (10)	0·205 (4)	0·249 (13)	3 (2)	O(7)
H(2)	−0·053 (8)	0·253 (4)	0·484 (10)	2 (1)	C(2)
H(3)	0·094 (9)	0·264 (5)	0·025 (12)	3 (2)	C(4)
H(4)	−0·044 (9)	0·304 (4)	0·097 (12)	3 (2)	C(4)
H(*W*1*a*)	0·824 (12)	−0·008 (7)	0·436 (16)	6 (3)	O(*W*1)
H(*W*1*b*)	0·856 (11)	0·054 (6)	0·476 (15)	5 (3)	O(*W*1)
H(*W*2*a*)	0·468 (13)	0·089 (6)	0·130 (15)	5 (3)	O(*W*2)
H(*W*2*b*)	0·561 (17)	0·083 (8)	0·220 (19)	5 (5)	O(*W*2)
H(*W*3*a*)	0·725 (12)	−0·086 (5)	0·836 (13)	5 (2)	O(*W*3)
H(*W*3*b*)	0·638 (11)	−0·028 (5)	0·810 (14)	4 (3)	O(*W*3)
H(*W*4)	0·031 (8)	0·036 (3)	0·765 (10)	2 (1)	O(*W*4)
H(*W*5)	0·553 (9)	0·020 (6)	0·505 (12)	4 (2)	O(*W*5)

Table 2. *Observed and calculated structure factors*

Each entry lists, in order, k, $|F_o|$, $|F_c|$, $\sigma|F_o|$ and α (phase angle in multiples of π radians). Unobserved reflections are denoted by an asterisk. The 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	$\lvert F_o\rvert$	$\lvert F_c\rvert$	$\sigma\lvert F_o\rvert$	α
(0,k,0)				
2	22.6	18.6	.3	.00
4	12.2	12.0	.2	.00
6	29.8	28.9	.2	.00
8	68.8	70.1	.7	1.00
10	9.8	8.0	.3	1.00
12	35.0	35.8	.3	1.00
14	26.4	26.6	.3	1.00
16	12.3	11.7	.3	.00
18	8.9	8.7	.3	.00
20	13.6	12.6	.2	.00
22	21.0	21.3	.2	.00
(0,k,1)				
0	24.0	22.3	.2	.00
1	35.0	33.6	.4	.50
2	85.5	80.7	1.1	.00
3	5.5	2.1	.3	.50
4	16.2	16.3	.2	1.00
5	44.7	43.0	.3	1.50
6	52.8	53.6	.4	1.00
7	8.5	8.7	.2	1.50
8	47.7	48.5	.4	1.00
9	48.6	48.8	.4	1.50
10	67.5	65.3	.5	1.00
11	14.8	14.2	.2	1.50
12	17.9	19.4	.3	1.00
13	26.1	24.7	.3	.50
14	9.7	9.7	.4	.00
15	15.1	10.5	.3	1.50
16	3.6	1.9*	.5	.00
17	22.9	22.2	.3	1.50
18	15.4	16.1	.3	.00
19	2.8	1.7*	.4	.50
20	13.8	13.7	.2	.00
21	2.0	2.0*	.3	.50
(0,k,2)				
0	46.7	46.2	.3	1.00
1	65.3	64.3	.4	.50
2	73.8	73.9	.7	.00
3	57.1	54.6	.6	1.50
4	85.6	83.1	.8	.00
5	33.8	32.2	.3	1.50
6	59.8	57.5	.4	1.00
7	44.3	44.4	.3	1.50
8	3.8	2.3	.4	.00
9	41.1	41.6	.3	1.50
10	26.0	25.0	.3	1.00
11	28.5	27.5	.3	.50
12	20.6	21.5	.3	1.00
13	19.8	20.0	.3	1.50
14	19.3	20.6	.3	1.00
15	9.0	7.3	.4	.50
16	9.2	8.5	.3	1.00
17	3.5	1.3*	.5	1.50
18	16.1	16.7	.2	.00
19	10.8	11.4	.2	.50
20	12.3	11.9	.2	.00
21	9.8	9.6	.2	.50
(0,k,3)				
0	107.9	110.2	.9	1.00
1	26.1	27.2	.2	.50
2	14.8	15.6	.2	1.00
3	88.3	92.9	.8	.50
4	19.9	17.9	.6	.00
5	17.4	16.9	.2	1.50
6	17.9	17.8	.2	.00
7	26.0	26.0	.3	1.50
8	19.0	19.2	.2	1.00
9	28.9	28.5	.3	1.50
10	6.5	8.0	.4	1.00
11	36.1	35.8	.3	1.50
12	17.2	17.3	.3	1.00
13	15.7	16.6	.3	1.50
14	13.5	13.5	.3	1.00
15	7.1	7.2	.4	1.50
16	3.5	2.1*	.5	1.00
17	8.0	7.8	.3	.50
18	3.0	1.3*	.4	1.00
19	6.4	7.4	.3	1.50
20	16.3	11.5	.3	.00
(0,k,4)				
0	7.4	7.5	.3	1.00
1	61.5	63.1	.3	.50
2	60.2	62.5	.4	1.00
3	27.4	28.8	.3	.50
4	26.6	25.1	.3	1.00
5	3.2	3.6*	.4	1.50
6	62.5	63.1	.4	.00
7	5.0	5.7	.5	1.50
8	9.3	8.0	.3	.00
9	7.7	6.5	.4	1.50
10	7.9	7.9	.5	.00
11	20.6	21.0	.3	1.50
12	4.9	1.5	.5	1.00
13	30.5	31.5	.3	1.50
14	3.6	.0*	.5	.00
15	6.3	5.8	.4	.50
16	8.1	6.9	.3	.00
17	18.0	16.2	.4	.50
18	5.4	5.6	.3	1.00
19	28.7	29.2	.2	.50
(0,k,5)				
0	19.8	18.8	.3	.00
1	19.2	21.3	.3	.50
2	15.5	13.3	.3	1.00
3	25.2	25.1	.3	.50
4	29.0	29.8	.3	1.00
5	25.7	26.5	.3	.50
6	32.4	32.7	.3	.00
7	3.7	.2*	.3	.50
8	33.0	33.4	.3	.00
9	21.6	21.7	.3	1.50
10	20.2	20.6	.3	.00
11	46.6	49.3	.4	1.50
12	14.8	15.6	.3	.00
13	3.2	.0*	.3	1.50
14	4.5	4.6	.3	1.00
15	11.2	11.3	.3	1.50
16	2.8	3.7*	.4	.00
17	6.8	6.3	.2	.50
18	1.7	6.0*	.3	1.00
(0,k,6)				
0	45.5	42.4	.5	1.00
1	25.5	25.3	.3	.50
2	3.3	3.6	.5	1.00
3	9.2	7.4	.4	1.50
4	7.8	7.9	.4	1.00
5	27.1	25.0	.5	.50
6	19.3	17.9	.3	1.00
7	7.4	5.7	.4	1.50
8	28.3	29.2	.3	.00
9	15.1	17.2	.3	1.50
10	13.7	14.0	.3	.00
11	10.8	10.2	.3	1.50
12	24.4	24.5	.3	.00
13	19.6	19.8	.2	1.50
14	26.6	26.8	.2	.00
15	2.2	2.1*	.3	1.50
16	1.8	.7*	.3	.00
(0,k,7)				
0	7.2	5.6	.5	.00
1	3.7	3.5*	.5	1.50
2	17.4	17.1	.3	1.00
3	4.5	6.1	.6	1.50
4	11.8	10.9	.3	.00
5	5.9	3.7	.4	1.50
6	6.6	6.3	.4	1.00
7	7.6	8.0	.3	1.50
8	4.9	5.0	.5	.00
9	6.3	6.1	.3	1.50
10	36.9	35.0	.3	.00
11	7.4	5.9	.3	1.50
12	17.5	16.9	.2	.00
13	7.0	.9*	.3	.50
14	6.7	6.2	.2	.00
(0,k,8)				
0	22.4	21.4	.3	1.00
1	7.9	9.8	.3	1.50
2	18.6	16.7	.2	1.00
3	16.1	14.9	.2	.50
4	5.9	4.3	.3	1.00
5	15.4	15.2	.2	1.50
6	2.5	.2*	.4	.00
7	2.4	1.7*	.4	.50
8	4.6	3.2	.3	1.00
9	7.1	7.1	.2	.50
10	7.6	7.5	.2	.00
(0,k,9)				
0	1.8	4.7*	.3	.00
1	7.3	7.1	.2	1.50
2	16.0	15.7	.2	1.00
3	18.0	17.7	.2	1.50
(1,k,0)				
1	61.4	55.6	.6	.00
2	21.7	20.9	.2	.00
3	24.6	23.9	.2	1.00
4	44.7	41.3	.3	.00
5	6.2	4.8	.3	.00
6	59.1	59.1	.4	.00
7	3.8	3.6	.5	.00
8	27.0	27.7	.2	.00
9	13.1	13.0	.2	1.00
10	25.6	23.4	.3	.00
11	4.7	2.6	.4	1.00
12	8.2	13.3	.4	.00
13	8.1	9.3	.4	1.00
14	25.1	23.9	.3	1.00
15	3.5	.0*	.5	1.00
16	29.6	30.3	.3	1.00
17	11.0	11.0	.3	.00
18	3.2	3.2*	.5	1.00
19	4.0	2.7	.6	.00
20	4.4	3.7	.4	1.00
21	4.7	3.6	.3	.00
(1,k,1)				
0	74.4	75.1	.6	.50
1	13.5	14.4	.2	1.59
2	48.6	46.1	.4	1.67
3	45.7	42.3	.4	.08
4	35.2	32.1	.3	.35
5	83.3	81.0	1.2	.41
6	13.1	11.8	.2	.36
7	63.4	59.5	.4	.65
8	39.9	34.1	.3	1.57
9	32.8	32.6	.3	1.20
10	23.1	21.0	.2	1.49
11	14.4	12.0	.3	.41
12	21.1	21.8	.3	1.25
13	11.8	10.7	.3	.59
14	16.8	18.0	.3	.96
15	31.1	34.6	.3	1.77
16	37.0	36.6	.3	.98
17	19.3	18.9	.3	1.33
18	9.1	8.2	.3	1.16
19	8.8	9.4	.3	1.74
20	6.2	6.7	.2	1.35
21	5.4	6.3	.2	.17
(1,k,2)				
0	48.2	46.2	.3	.50
1	10.3	10.2	.2	1.72
2	22.0	21.3	.2	1.91
3	25.2	25.3	.2	.29
4	38.8	36.7	.3	1.71
5	75.0	75.3	.8	.73
6	64.2	59.5	.4	1.89
7	39.1	39.0	.3	.57
8	40.8	40.7	.3	1.74
9	5.7	5.1	.3	1.05
10	28.0	28.2	.3	1.65
11	19.0	19.0	.3	1.22
12	24.3	23.0	.3	1.23
13	23.9	23.3	.3	1.48
14	21.3	22.3	.3	1.17
15	36.5	38.6	.3	1.25
16	11.9	11.5	.3	.09
17	26.2	27.0	.3	1.66
18	30.3	29.8	.3	.87
19	15.5	14.7	.2	1.51
20	7.7	8.0	.2	1.25
21	6.4	7.7	.2	.35
(1,k,3)				
0	26.2	27.3	.2	.50
1	22.5	23.6	.2	.47
2	33.9	34.9	.3	.54
3	87.9	87.4	.9	.49
4	73.9	71.8	.3	.30
5	27.1	27.7	.3	.50
6	27.6	25.0	.3	1.64
7	43.6	44.3	.4	.63
8	18.8	18.8	.3	1.90
9	60.2	59.5	.4	.51
10	23.1	23.5	.3	1.50
11	11.3	10.3	.3	1.23
12	23.1	21.9	.3	1.19
13	19.0	18.7	.3	1.27
14	12.3	10.4	.3	.63
15	25.6	25.9	.3	1.62
16	6.2	6.7	.3	1.17
17	26.4	24.8	.3	1.62
18	7.8	8.6	.3	1.11
19	7.3	7.6	.2	1.78
20	7.6	7.7	.2	.54
(1,k,4)				
0	4.8	5.0	.3	.50
1	35.8	35.2	.3	.53
2	33.5	35.1	.3	.45
3	23.1	23.6	.3	.74
4	18.9	18.8	.2	1.59
5	28.3	28.1	.3	.29
6	16.1	15.4	.3	1.40
7	27.3	27.6	.3	.68
8	5.7	4.5	.3	1.18
9	12.6	12.3	.3	.22
10	19.9	18.8	.3	1.02
11	14.6	14.4	.3	.96
12	8.7	8.3	.3	1.88
13	40.9	41.1	.4	1.48
14	13.8	12.1	.3	1.45
15	20.9	21.6	.3	1.51
16	13.0	11.5	.3	1.08
17	8.7	6.8	.3	1.28
18	21.3	21.1	.2	.29
19	16.9	17.5	.2	1.57
(1,k,5)				
0	27.4	28.7	.3	.50
1	6.9	6.7	.4	1.82
2	6.5	7.9	.5	1.90
3	24.1	26.5	.3	.66
4	28.4	27.3	.3	.49
5	33.3	33.3	.3	.44
6	19.6	16.3	.3	.45
7	21.6	21.5	.3	.25
8	14.5	13.6	.3	1.19
9	7.9	6.9	.3	.38
10	5.4	4.0	.4	.18
11	3.3	2.4*	.5	1.86
12	18.4	19.7	.3	1.94
13	6.3	5.7	.4	1.61
14	3.4	1.6*	.5	1.53
15	13.9	13.2	.2	1.35
16	16.4	16.0	.2	.13
17	14.4	13.3	.2	1.70
18	9.7	8.8	.2	1.94
(1,k,6)				
0	8.7	6.7	.4	1.50
1	13.9	14.1	.3	1.05
2	14.2	14.0	.3	.86
3	7.9	7.4	.5	1.92
4	25.4	22.5	.3	1.21
5	20.6	20.6	.3	.40
6	38.4	38.0	.3	.90
7	17.3	16.6	.3	.23
8	16.8	17.9	.3	1.06
9	6.6	6.3	.6	1.69
10	3.7	4.0*	.5	1.16
11	12.2	11.2	.3	1.76
12	7.3	7.1	.3	1.64
13	12.9	13.8	.2	.13
14	17.4	16.9	.2	1.85
15	10.4	11.9	.2	1.93
16	11.6	11.5	.2	.11
(1,k,7)				
0	10.7	9.9	.3	1.50
1	7.1	6.6	.4	.96
2	22.1	21.4	.3	1.07
3	3.3	3.0	.6	1.29
4	20.6	20.1	.3	1.06
5	10.9	12.1	.3	1.25
6	18.6	17.9	.3	1.03
7	6.7	4.2	.5	1.79
8	11.1	10.3	.3	.86
9	13.0	12.2	.3	1.81
10	9.2	11.2	.2	1.66
11	12.3	13.6	.4	1.91
12	5.5	3.2	.3	.05
13	5.1	4.8	.2	.10
(1,k,8)				
0	16.1	16.0	.2	1.50
1	12.6	12.1	.3	.81
2	13.3	12.7	.2	.93
3	4.0	3.5	.5	1.11
4	22.4	20.9	.2	.96
5	9.6	10.3	.2	1.55
6	19.8	19.1	.2	1.08
7	5.5	4.5	.3	1.31
8	12.1	11.3	.2	.99
9	4.2	4.1	.3	.33
10	3.9	3.7	.2	1.02
(1,k,9)				
0	8.6	8.5	.2	.50
1	9.6	9.7	.2	1.34
2	11.3	11.2	.1	1.39
(2,k,0)				
0	36.7	31.4	.4	1.00
1	96.7	86.8	1.2	1.00
2	28.4	28.7	.2	1.00
3	44.4	43.1	.5	.00
4	27.8	26.1	.2	.00
5	56.6	56.4	.4	.00
6	64.7	57.6	.4	1.00
7	76.4	73.8	.5	.00
8	43.7	42.6	.3	.00
9	65.1	63.6	.5	.00
10	66.1	63.3	.5	.00
11	20.2	19.3	.3	1.00
12	53.7	53.3	.4	.00
13	15.0	14.0	.3	1.00
14	22.2	21.7	.3	.00
15	27.8	25.9	.3	1.00
16	3.5	3.4*	.5	1.00
17	32.2	31.1	.3	1.00
18	4.5	3.4	.5	.00
19	5.8	5.8	.4	1.00
20	12.6	11.0	.2	1.00
21	2.0	3.5*	.3	.00
(2,k,1)				
0	40.2	39.2	.3	1.00
1	47.8	48.9	.4	1.96
2	36.5	36.2	.3	.71
3	57.9	51.6	.4	1.57
4	77.9	75.3	.7	1.51
5	27.6	28.7	.2	1.73
6	43.6	42.7	.3	.61
7	77.4	71.0	.7	1.77
8	23.7	24.9	.3	.52
9	16.1	14.3	.2	.33
10	37.6	36.0	.3	1.99
11	22.9	20.8	.3	.37
12	32.5	33.2	.3	.25
13	20.9	21.6	.3	1.26
14	21.9	21.1	.3	1.90
15	46.2	44.1	.4	.85
16	28.0	27.6	.3	1.41
17	22.1	21.5	.3	1.08
18	20.3	20.0	.5	.95
19	16.2	16.3	.2	1.32
20	16.6	15.4	.2	.92
21	8.7	9.3	.2	1.79
(2,k,2)				
0	32.4	30.6	.3	.00
1	31.9	30.0	.2	.55
2	70.6	75.1	1.2	1.25
3	37.6	39.4	.3	.05
4	45.5	44.8	.4	1.04
5	65.1	60.6	.4	1.68
6	18.8	18.8	.2	.10
7	21.3	20.1	.2	.28
8	38.3	36.8	.3	.15
9	19.3	19.9	.3	.28
10	16.9	16.1	.3	.38
11	24.4	23.5	.3	.47
12	27.9	26.6	.3	1.68
13	19.2	20.3	.3	.99
14	5.9	5.0	.5	1.48
15	8.7	7.5	.3	1.03
16	24.6	25.1	.3	1.58
17	10.3	10.5	.3	1.67
18	5.5	5.1	.3	1.39
19	17.6	17.0	.2	1.28
20	11.7	11.8	.2	.99
21	19.0	17.9	.2	1.46
(2,k,3)				
0	42.7	43.7	.3	1.00
1	39.7	41.3	.4	1.58
2	19.3	20.6	.2	.63
3	27.3	29.1	.3	1.79
4	37.5	38.3	.3	.76
5	25.7	24.5	.2	1.68
6	25.7	25.3	.2	.32
7	25.0	27.1	.3	.85
8	12.0	11.4	.3	.26
9	3.4	6.0*	.5	1.39
10	29.1	31.3	.3	.65
11	11.3	11.9	.3	.51
12	12.0	11.3	.3	.99
13	43.2	42.7	.4	.56
14	22.2	22.2	.3	1.44
15	11.3	9.9	.4	.01
16	8.6	7.5	.3	1.51
17	6.5	6.4	.3	1.62
18	18.5	17.1	.2	1.44
19	10.9	10.1	.2	1.42
20	2.2	3.4*	.3	1.04
(2,k,4)				
0	22.5	21.4	.2	1.00
1	10.0	10.5	.2	1.76
2	14.2	14.7	.3	.09
3	2.9	3.5*	.4	1.22
4	32.2	32.0	.4	.32
5	29.0	26.5	.3	.66
6	13.0	12.3	.3	.58
7	30.3	30.9	.1	.68
8	12.6	12.8	.3	.71
9	25.5	26.7	.3	.71
10	11.4	11.5	.3	.68
11	33.2	36.5	.3	.62
12	34.6	34.7	.3	1.33
13	13.2	14.1	.3	.18
14	14.3	14.8	.3	1.31
15	12.7	12.2	.3	.05
16	6.8	6.2	.4	1.37
17	7.9	7.3	.3	1.58
18	10.7	9.8	.2	1.45
19	9.1	9.6	.2	1.95
(2,k,5)				
0	10.7	8.9	.3	.00
1	36.5	37.9	.3	1.61
2	44.1	47.8	.4	.42
3	29.8	30.2	.3	1.25
4	19.6	20.0	.3	.34
5	23.4	23.3	.3	.60
6	29.0	28.4	.3	.52
7	6.9	3.7	.4	1.20
8	21.1	22.3	.3	.77
9	27.7	29.1	.3	.60
10	16.5	18.0	.3	1.50
11	10.6	10.0	.3	.51
12	10.6	10.0	.3	.65
13	17.4	16.3	.3	.15
14	16.9	16.6	.2	1.54
15	16.3	17.8	.2	.15
16	12.5	12.4	.2	1.68
17	8.8	7.8	.2	.10
(2,k,6)				
0	27.1	27.7	.3	.00
1	13.6	13.8	.3	1.68
2	24.4	25.3	.3	.10
3	24.6	25.2	.3	1.06
4	23.0	23.7	.3	.16
5	27.3	28.0	.3	1.12
6	17.4	17.1	.3	.41
7	17.6	18.3	.3	.67
8	16.6	16.2	.3	.74
9	25.8	25.5	.3	.75
10	21.7	22.8	.3	1.18
11	8.5	9.3	.3	.11
12	8.0	5.9	.3	1.25
13	11.8	11.2	.2	.01
14	2.7	2.7*	.4	.76
15	2.2	1.4*	.3	.45
16	15.1	14.7	.1	1.43
(2,k,7)				
0	28.2	29.9	.3	.00
1	25.9	25.5	.3	1.00
2	15.6	14.9	.3	1.84
3	8.7	7.6	.3	1.72
4	10.3	11.9	.3	.60
5	15.9	15.7	.2	1.09
6	11.2	11.5	.3	.95
7	18.3	16.9	.2	.95
8	5.0	4.8	.4	1.69
9	15.1	14.1	.2	.01
10	13.8	13.4	.2	.98
11	11.1	9.3	.2	1.61
12	4.9	4.1	.3	1.09
13	4.9	4.7	.2	.51
(2,k,8)				
0	12.3	12.5	.2	.00
1	3.2	1.5*	.4	1.89
2	4.6	4.3	.4	.18
3	7.7	7.4	.3	1.10
4	11.9	11.6	.2	1.67
5	15.3	15.0	.2	1.02
6	5.1	4.9	.3	1.15
7	13.8	13.3	.2	1.21
8	14.1	15.2	.2	1.03
9	11.3	12.5	.2	1.49
(3,k,0)				
1	49.3	50.6	.5	1.00
2	29.6	28.7	.2	1.00
3	37.5	38.0	.3	1.00
4	65.8	67.5	.7	1.00
5	8.1	4.8	.3	1.00
6	5.3	4.7	.3	.00
7	5.0	2.3	.4	.00
8	8.0	8.3	.3	1.00
9	64.0	62.5	.4	.00
10	29.0	28.1	.3	1.00
11	25.1	25.3	.3	.00
12	3.4	1.3*	.5	.00
13	13.7	12.0	.3	.00
14	14.8	15.3	.3	.00
15	13.2	12.9	.3	.00
16	9.8	9.3	.3	.00
17	3.8	2.3	.6	1.00
18	5.8	6.6	.4	1.00
19	2.6	.0*	.4	.00
20	3.4	2.7	.4	.00
21	6.9	8.3	.2	1.00
(3,k,1)				
0	71.6	75.6	.7	1.50
1	17.6	18.2	.2	.82
2	57.1	60.5	.6	1.53
3	46.9	42.6	.3	.27
4	19.4	19.3	.2	.91
5	56.0	57.3	.6	1.58
6	17.1	17.0	.2	1.18
7	46.4	46.6	.4	1.89
7	45.8	46.4	.5	1.89
8	19.5	19.3	.2	.74
9	19.6	19.7	.2	.23
10	27.6	25.5	.3	.33
11	31.6	30.3	.3	1.94
12	13.3	11.8	.3	.11
13	23.0	23.0	.3	.22
14	33.2	32.6	.3	.21
15	7.5	6.6	.5	1.64
16	16.2	14.5	.3	1.16
17	10.0	10.3	.3	1.27
18	14.7	14.2	.2	1.70
19	15.5	15.0	.2	.82
20	3.8	4.1	.3	.09
(3,k,2)				
0	61.4	67.4	.6	1.50
1	38.2	41.0	.3	1.03
2	60.7	60.8	.4	1.31
3	55.6	56.5	.4	1.10
4	16.1	15.9	.2	1.64
5	19.9	19.9	.2	1.30
6	19.6	19.0	.2	.97
7	10.1	8.8	.3	.71
8	27.6	28.2	.3	.64
9	23.2	23.3	.3	.06
10	39.7	38.6	.3	.38
11	21.0	20.8	.3	.23
12	11.7	10.2	.3	.64
13	11.3	10.8	.3	.19
14	14.9	16.7	.3	.04
15	5.9	5.1	.4	.19
16	23.5	22.3	.3	1.83
17	12.3	11.1	.3	.64
18	16.8	16.3	.2	1.61
19	14.3	16.8	.2	1.12
20	16.1	15.0	.2	1.32
(3,k,3)				
0	56.9	61.1	.4	1.50
1	28.4	29.3	.3	1.25
2	44.1	44.7	.4	1.56
3	23.6	23.8	.2	1.23
4	23.0	23.4	.2	1.53
5	27.6	27.1	.3	1.30
6	21.0	21.3	.2	.68
7	17.6	17.6	.3	1.70
8	38.4	38.5	.3	.53
9	25.7	26.0	.3	1.55
10	17.1	17.2	.3	.38
11	12.0	12.9	.3	.32
12	32.7	34.1	.4	.32
13	13.3	13.3	.3	.16
14	10.0	10.1	.3	.84
15	5.1	4.9	.4	1.32
16	8.9	10.7	.3	.13
17	6.9	6.7	.3	.78
18	7.7	8.1	.2	.04
19	9.0	9.6	.7	.94
(3,k,4)				
0	4.9	3.6	.5	.50
1	23.3	23.4	.2	1.54
2	33.1	35.4	.3	1.69
3	28.7	28.2	.3	1.43
4	18.7	19.4	.3	1.54
5	14.8	13.3	.3	.33
6	20.7	21.0	.3	.41
7	4.5	6.7	.4	1.70
8	30.1	24.1	.3	.23
9	7.3	7.0	.5	.44
10	44.1	49.2	.4	.64
11	2.9	4.7*	.5	1.40
12	10.6	11.7	.3	.35
13	3.4	3.8*	.5	1.52
14	10.7	11.0	.3	.38
15	19.4	19.6	.2	.61
16	3.0	2.8*	.4	.42
17	11.8	11.9	.2	.55
18	18.2	17.7	.2	1.49
(3,k,5)				
0	70.1	19.8	.3	1.50
1	8.2	7.5	.3	.20
2	12.4	13.3	.3	1.26
3	8.4	9.2	.4	.36
4	11.8	12.0	.3	.11
5	18.7	17.9	.3	1.56
6	11.2	9.9	.3	.01
7	21.5	21.7	.3	1.18
8	20.4	21.7	.3	.50
9	4.4	2.8	.3	1.72
10	21.8	23.0	.3	.75
11	10.2	10.0	.3	1.29
12	17.3	16.7	.3	.62
13	11.5	11.5	.3	.85
14	19.9	18.8	.2	.43
15	8.8	9.2	.3	.27
16	3.2	2.7	.3	1.32
17	1.9	2.9*	.5	1.98
(3,k,6)				
0	22.2	22.4	.3	1.50
1	29.0	32.5	.3	.23
2	10.2	11.1	.3	.06
3	36.2	35.9	.3	1.92
4	14.6	14.4	.3	1.87
5	4.3	4.9	.5	1.87
6	10.9	11.6	.3	1.92
7	5.2	4.3	.4	1.89
8	3.0	.7*	.5	1.12
9	19.2	19.8	.3	1.14
10	11.4	10.4	.3	.27
11	15.3	15.5	.2	1.04
12	10.2	10.4	.2	.15
13	5.1	5.0	.4	.77
14	2.3	2.4*	.3	.80
15	7.4	8.1	.2	.88
(3,k,7)				
0	3.0	1.2*	.5	1.50
1	22.0	23.1	.3	1.96
2	3.2	3.5	.5	.62
3	7.3	6.6	.3	.26
4	3.6	2.4	.6	.54
5	5.7	6.3	.4	.57
6	7.3	6.4	.3	1.89
7	11.1	9.8	.2	1.14
8	3.2	2.5*	.4	1.54
9	17.7	17.4	.2	1.06
10	15.0	13.7	.2	1.80
11	20.5	19.4	.2	.90
12	9.9	7.7	.1	.89
(3,k,8)				
0	6.9	8.1	.3	.50
1	22.1	20.5	.2	1.98
2	8.6	8.2	.2	1.91
3	8.6	8.1	.2	.02
4	5.5	5.9	.3	1.64
5	4.3	4.2	.4	.07
6	1.7	2.9*	.3	.63
7	6.0	5.5	.2	1.18
8	12.5	12.1	.2	1.69
(4,k,0)				
0	2.2	1.3*	.3	.00
1	56.9	57.2	.6	1.00
2	20.4	20.2	.2	.00
3	92.1	96.6	1.4	1.00
4	15.6	14.4	.2	.00
5	82.3	92.4	.8	1.00
6	3.9	1.7	.4	1.00
7	18.0	18.9	.2	1.00
8	52.1	51.4	.5	.00
9	28.1	29.2	.3	1.00
10	9.8	10.6	.3	.00
11	14.0	13.9	.3	.00
12	10.5	10.5	.3	1.00
13	7.9	7.5	.3	.00
14	17.6	16.6	.3	.00
15	12.9	11.8	.3	.00
16	4.7	3.7	.5	1.00
17	35.0	33.2	.3	.00
18	3.0	1.9*	.4	1.00
19	3.3	4.4	.5	.00
20	8.4	9.4	.2	.00
(4,k,1)				
0	9.5	9.0	.2	1.00
1	26.4	26.3	.2	1.22
2	59.9	58.3	.6	1.36
3	33.5	33.6	.3	1.00
4	10.0	11.0	.2	1.00
5	55.4	55.7	.4	.90
6	35.4	36.1	.3	1.61
7	42.0	43.1	.4	1.15
8	9.8	9.3	.3	1.08
9	16.6	17.6	.2	1.65
10	19.5	21.5	.3	.30
11	19.7	18.5	.3	1.92
12	8.4	8.5	.3	1.50
13	31.5	31.5	.3	1.98
14	7.7	8.3	.3	.64
15	17.6	17.5	.3	1.83
16	3.6	6.6*	.5	1.69
17	19.3	18.2	.2	1.78
18	4.5	4.6	.4	.49
19	15.5	16.2	.2	.16
20	5.5	5.7	.2	.41
(4,k,2)				
0	16.6	16.7	.2	1.00
1	24.4	26.5	.2	1.24
2	34.9	36.7	.3	1.59
3	32.1	31.1	.3	.70
4	48.3	50.4	.4	1.53
5	30.2	31.3	.3	1.10
6	11.6	9.8	.2	.50
7	20.8	21.2	.2	1.05
8	3.6	3.0*	.4	.12
9	13.3	13.6	.3	1.08
10	27.6	23.8	.3	.62
11	15.3	11.3	.3	1.24
12	17.9	16.9	.3	.04
13	4.7	4.4	.5	1.84
14	17.3	17.6	.3	.74
15	27.6	26.3	.3	1.95
16	14.5	14.0	.2	.56
17	12.3	11.4	.2	1.90
18	11.3	10.7	.2	.35
19	7.8	8.6	.2	.45
(4,k,3)				
0	6.3	4.8	.3	.00
1	28.4	27.9	.3	.14
2	9.2	8.9	.3	.88
3	16.4	17.9	.2	1.64
4	34.7	37.0	.4	1.46
5	14.9	14.1	.2	.22
6	39.9	40.5	.3	1.50
7	9.7	10.4	.3	1.04
8	34.8	34.3	.3	1.28
9	17.7	18.1	.3	1.09
10	11.5	10.8	.3	1.43
11	5.7	4.0	.4	1.11
12	19.3	19.6	.3	.55
13	16.6	14.1	.4	1.64
14	11.9	9.6	.3	.61
15	9.5	10.1	.3	1.91
16	6.6	6.6	.3	.56
17	7.5	8.3	.2	.40
18	12.4	12.5	.2	.71
19	12.4	10.9	.2	1.60
(4,k,4)				
0	15.3	13.7	.2	.00
1	20.2	22.6	.3	.20
2	17.9	19.5	.2	1.45
3	22.3	23.3	.3	.08
4	20.9	22.1	.3	1.44
5	30.6	30.2	.3	1.83
6	19.6	20.0	.3	1.38
7	32.9	25.2	.3	.38
8	18.3	18.4	.3	1.41
9	8.7	11.0	.3	.65
10	3.7	1.6*	.5	1.13
11	2.9	3.7*	.5	1.44
12	8.6	10.5	.3	.84
13	6.3	6.3	.4	.43
14	28.7	28.5	.3	.45
15	8.3	8.4	.3	.73
16	21.6	21.1	.2	.52
17	8.1	6.6	.2	.57
18	16.6	16.4	.2	.58
(4,k,5)				
0	3.4	3.6*	.5	1.00
1	5.4	5.1	.4	.52
2	24.3	27.7	.3	1.81
3	18.4	18.4	.2	1.73
4	8.0	5.9	.3	.21
5	25.2	27.1	.3	.19
6	43.1	44.8	.4	1.63
7	11.4	10.4	.3	1.77
8	23.9	25.0	.3	1.49
9	8.1	8.1	.3	.15
10	14.4	14.1	.3	1.63
11	12.1	11.9	.3	.84
12	12.4	12.6	.2	.60
13	20.7	19.7	.2	.95
14	15.3	15.1	.2	.42
15	8.9	8.7	.2	.79
16	18.9	17.7	.2	.53
(4,k,6)				
0	3.1	3.6*	.5	.00
1	10.6	12.5*	.5	1.75
2	6.9	6.9	.3	1.26
3	20.6	22.8	.3	.15
4	14.9	13.7	.3	1.30
5	19.3	19.5	.3	.01
6	9.5	11.1	.3	1.78
7	18.0	18.2	.2	1.92
8	16.1	15.7	.2	1.31
9	19.5	19.7	.2	.00
10	8.6	9.0	.2	1.62
11	12.2	9.9	.2	.40
12	8.6	8.4	.2	.09
13	8.8	7.9	.2	.80
14	8.6	9.4	.2	.73
(4,k,7)				
0	2.7	2.3*	.4	.00
1	13.4	12.5	.2	1.47
2	2.3	3.9*	.4	.70
3	7.4	7.3	.3	.32
4	4.8	5.8	.3	1.75
5	11.4	12.4	.2	1.75
6	3.9	4.3	.4	1.87
7	26.0	26.1	.2	1.94
8	8.1	8.2	.3	.24
9	4.4	3.3	.3	.36
10	4.1	4.8	.3	1.36
11	2.3	2.1	.3	1.41
(4,k,8)				
0	2.0	.0*	.3	.00
1	4.3	4.2	.3	.44
2	7.9	9.0	.2	.93
3	16.6	16.3	.2	1.78
4	3.9	3.4	.3	.84
5	10.5	10.9	.2	.00
6	1.9	2.2*	.2	.17
(5,k,0)				
1	25.6	28.0	.2	.00
2	28.6	28.7	.3	1.00
3	42.6	42.7	.3	.00
4	32.6	29.5	.3	.00
5	32.1	32.6	.3	.00
6	30.3	31.3	.3	1.00
7	28.5	28.3	.3	1.00
8	3.0	2.2*	.4	1.00
9	3.3	.2*	.5	1.00
10	23.0	22.7	.3	.00
11	30.7	29.8	.3	1.00
12	12.9	12.0	.3	1.00
13	30.2	30.9	.3	1.00
14	5.0	5.4	.5	.00
15	3.3	2.4*	.5	.00
16	12.9	12.1	.2	.00
17	5.2	5.8	.4	1.00
18	5.2	4.3	.3	.00
19	16.9	16.4	.2	.00
(5,k,1)				
0	2.4	2.7*	.4	.50
1	29.4	30.4	.2	1.77
2	32.3	30.9	.3	.30
3	16.1	16.8	.2	1.96
4	20.8	21.0	.2	.76
5	8.8	9.0	.3	1.69
6	14.8	14.7	.2	1.37
7	14.9	15.4	.2	1.41
8	28.7	27.6	.3	1.06
9	21.2	22.6	.3	1.24
10	17.6	19.1	.3	1.84
11	19.8	19.2	.3	.82
12	22.4	21.5	.3	1.56
13	16.3	15.1	.3	.74
14	18.2	18.1	.3	1.56
15	7.6	6.6	.3	.84
16	3.3	4.2*	.4	1.60
17	15.9	16.3	.2	.16
18	7.7	7.8	.2	.35
19	19.4	19.2	.2	1.91
(5,k,2)				
0	5.1	3.9	.4	1.50
1	34.7	35.3	.3	1.73
2	11.5	12.1	.2	.82
3	20.3	20.5	.2	1.45
4	27.2	29.9	.3	1.01
5	22.5	22.1	.2	1.33
6	14.5	17.4	.2	1.62
7	17.1	18.7	.3	1.59
8	26.4	28.3	.3	1.72
9	29.9	29.0	.3	1.00
10	36.2	34.6	.3	1.21
11	25.8	27.3	.3	1.11
12	32.6	33.1	.3	1.58
13	14.1	13.3	.3	.61
14	16.2	16.1	.2	1.77
15	18.5	18.4	.2	.74
16	2.5	3.6*	.4	.30
17	11.1	11.4	.2	.29
18	8.7	8.1	.2	.39
(5,k,3)				
0	57.0	61.1	.4	.50
1	17.1	19.5	.2	.15
2	31.7	34.9	.3	.61
3	10.8	8.3	.2	1.25
4	19.4	21.0	.2	.73
5	35.1	34.3	.3	1.49
6	21.0	20.2	.2	.46
7	13.2	16.3	.3	1.25
8	18.3	17.6	.3	1.44
9	19.7	19.9	.3	1.21
10	33.2	33.8	.3	1.38
11	22.4	20.5	.3	.59
12	16.0	16.4	.2	1.61
13	9.9	9.1	.3	.82
14	19.8	20.3	.2	1.62
15	8.1	8.7	.3	.43
16	2.1	2.1*	.4	1.61
17	7.7	7.6	.2	.56
18	10.7	10.3	.1	.39
(5,k,4)				
0	13.4	13.9	.3	.50
1	5.1	5.5	.4	1.20
2	22.2	24.5	.3	.69
3	21.4	23.7	.3	1.41
4	18.1	17.5	.3	.06
5	13.5	13.5	.2	1.50
6	19.6	18.7	.3	1.10
7	20.0	18.9	.2	1.07
8	17.0	16.7	.3	1.38
9	4.5	4.5	.4	.27
10	27.7	28.3	.3	1.57
11	16.7	14.3	.2	1.72
12	13.2	11.3	.3	1.54
13	10.0	10.2	.2	.53
14	7.1	7.8	.3	.95
15	9.5	10.2	.2	.13
16	12.5	11.1	.2	.12
17	7.7	7.8	.1	.70
(5,k,5)				
0	28.3	30.6	.3	.50
1	11.4	11.3	.3	1.05
2	21.8	23.3	.3	.43
3	13.2	14.6	.2	1.95
4	18.0	19.1	.2	.36
5	8.4	8.8	.3	1.13
6	10.6	10.0	.3	1.20
7	7.5	6.9	.3	1.83
8	11.3	11.5	.3	1.64
9	17.8	17.3	.2	1.83
10	8.3	7.4	.3	1.72
11	10.9	11.1	.2	.29
12	10.0	10.5	.2	1.31
13	11.5	11.4	.2	.09
14	6.2	4.0	.3	1.16
15	1.4	1.2*	.3	.26
(5,k,6)				
0	11.5	12.8	.2	.50
1	14.0	15.6	.2	1.04
2	22.0	22.5	.2	.07
3	17.1	17.7	.2	1.11
4	4.9	4.8	.3	.74
5	12.5	11.6	.2	.55
6	12.1	11.4	.2	1.76
7	20.7	20.4	.2	1.84
8	13.5	12.6	.2	1.49
9	13.5	13.3	.2	.16
10	2.2	.8*	.3	.35
12	7.2	8.1	.2	1.60
13	17.5	16.8	.2	1.92
(5,k,7)				
0	7.5	8.0	.3	1.50
1	15.2	15.3	.2	.89
2	2.8	3.4*	.4	.95
3	16.8	16.2	.2	.92
4	9.1	9.2	.2	1.76
5	6.8	7.0	.2	1.94
6	19.2	18.3	.2	1.85
7	10.9	11.3	.2	.07
8	11.4	11.8	.2	.11
9	16.7	16.5	.2	1.95
10	9.6	8.7	.1	1.22
(5,k,8)				
0	2.4	1.2	.3	1.50
1	18.8	17.3	.2	.88
2	4.0	4.6	.2	1.60
3	10.9	11.3	.1	.94
(6,k,0)				
0	25.3	26.9	.2	.00
1	12.5	11.0	.2	1.00
2	25.1	26.3	.2	.00
3	22.5	22.5	.2	.00
4	66.6	67.3	.4	.00
5	8.3	7.5	.3	.00
6	25.0	24.6	.3	.00
7	37.9	38.1	.3	.00
8	31.3	31.5	.3	1.00
9	30.3	30.2	.3	.00
10	16.6	14.5	.3	1.00
11	6.7	7.9	.3	1.00
12	27.7	27.1	.3	1.00
13	12.1	12.1	.3	1.00
14	9.0	9.7	.3	1.00
15	5.0	4.7	.4	1.00
16	9.2	9.4	.2	.00
17	5.2	5.3	.3	1.00
18	7.7	8.8	.2	.00
(6,k,1)				
0	14.5	15.0	.2	.00
1	8.7	8.7	.3	1.56
2	23.9	25.4	.2	.14
3	14.9	15.9	.2	1.90
4	14.9	15.8	.2	.37
5	15.0	15.2	.2	1.97
6	2.9	.1*	.4	1.47
7	6.4	5.4	.3	.94
8	20.0	18.7	.2	.79
9	12.9	13.3	.2	.10
10	36.5	35.6	.3	.76
11	20.6	20.3	.3	1.44
12	18.2	19.3	.3	1.15
13	18.3	20.1	.2	1.27
14	18.3	18.9	.2	1.17
15	13.7	14.7	.2	1.01
16	3.8	3.6	.4	.08
17	12.1	13.3	.2	.92
18	15.2	17.5	.2	1.84
(6,k,2)				
0	16.5	17.2	.2	.00
1	15.4	15.2	.2	1.91
2	22.3	23.3	.2	.06
3	3.2	2.1*	.4	1.79
4	6.1	3.8	.4	1.14
5	20.3	22.0	.3	.22
6	18.3	19.5	.2	.65
7	36.2	33.1	.4	.00
8	8.8	9.1	.3	.48
9	17.6	17.5	.2	1.06
10	20.5	20.0	.2	.91
11	25.0	27.2	.3	1.65
12	21.1	22.9	.3	1.30
13	12.2	12.2	.2	1.48
14	8.7	9.8	.2	1.36
15	15.3	13.4	.2	.96
16	13.5	13.8	.2	1.47
17	2.0	3.4*	.3	.61
(6,k,3)				
0	12.9	13.1	.2	.00
1	13.8	14.8	.2	.35
2	7.8	7.0	.3	.50
3	8.3	9.0	.3	.21
4	31.0	34.8	.3	.42
5	14.2	13.6	.3	.01
6	24.4	26.7	.3	.73
7	3.3	3.1*	.5	1.07
8	13.6	13.8	.2	.58
9	20.6	20.7	.2	1.31
10	9.8	8.0	.3	.59
11	11.8	11.6	.2	1.38
12	5.1	4.7	.4	.54
13	8.6	9.5	.3	1.71
14	6.6	6.3	.2	1.52
15	13.0	16.3	.2	1.44
16	16.0	17.8	.2	1.43
(6,k,4)				
0	3.0	4.4	.4	.00
1	20.7	22.6	.2	.57
2	17.9	20.0	.3	.79
3	22.9	22.2	.2	.44
4	5.9	4.6	.3	1.27
5	11.3	11.8	.3	.63
6	32.2	33.8	.3	.54
7	22.5	22.0	.2	1.23
8	9.6	10.8	.3	.90
9	13.3	14.0	.2	1.63
10	21.7	20.1	.2	1.76
11	11.2	11.4	.2	1.23
12	10.2	11.2	.2	1.90
13	5.4	4.7	.3	1.20
14	9.6	10.1	.2	1.55
15	7.4	8.4	.2	.07
(6,k,5)				
0	11.8	12.7	.2	1.00
1	24.6	24.3	.3	.41
2	12.6	12.9	.2	.75
3	19.6	19.6	.2	.68
4	28.5	27.9	.3	.43
5	11.6	12.3	.2	1.31
6	3.4	5.2*	.4	1.81
7	12.5	13.2	.2	1.59
8	16.4	16.1	.2	.35
9	9.8	9.9	.2	1.50
10	13.1	13.2	.2	.06
11	9.0	8.3	.2	1.66
12	11.5	11.5	.2	1.97
13	7.8	7.0	.2	1.49
14	10.9	12.4	.1	1.80
(6,k,6)				
0	21.5	22.3	.2	1.00
1	19.1	19.7	.2	.60
2	7.0	6.0	.2	.83
3	10.9	11.9	.2	.89
4	12.7	13.5	.2	.71
5	11.1	10.8	.2	1.06
6	2.8	4.3*	.4	.00
7	20.3	20.3	.2	1.08
8	19.9	20.0	.2	.07
9	11.7	11.2	.2	1.31
10	8.6	9.2	.2	.32
11	7.5	7.8	.1	1.63
(6,k,7)				
0	12.2	12.3	.2	1.00
1	7.5	8.0	.2	.91
2	8.9	8.7	.2	.95
3	9.7	9.4	.2	1.09
4	4.0	5.4	.2	1.48
5	13.7	13.2	.2	1.13
6	9.4	9.7	.1	1.93
7	2.9	4.0	.3	.09
(7,k,0)				
1	15.1	17.0	.2	1.00
2	14.1	14.3	.2	.00
3	22.2	23.1	.2	1.00
4	25.2	25.6	.3	.00
5	10.1	9.0	.2	1.00
6	23.9	24.6	.3	.00
7	22.3	22.5	.3	.00
8	26.2	24.8	.3	.00
9	8.3	8.0	.3	.00
10	11.8	11.4	.2	1.00
11	2.8	2.0*	.4	.00
12	10.2	10.9	.2	1.00
13	18.2	20.5	.2	.00
14	4.5	2.7	.3	1.00
15	2.3	.0*	.3	1.00
16	8.6	10.3	.2	1.00
(7,k,1)				
0	28.2	27.1	.3	.50
1	8.3	8.2	.3	.20
2	27.9	27.0	.3	1.69
3	36.5	34.9	.3	.62
4	31.6	31.7	.3	1.79
5	17.4	17.7	.2	.25
6	24.7	26.3	.3	.27
7	5.7	5.5	.4	.05
8	13.0	12.9	.3	1.49
9	26.5	27.2	.3	.19
10	7.7	6.5	.3	.20
11	9.0	9.6	.3	.00
12	12.7	13.7	.2	.99
13	13.7	14.6	.2	1.50
14	8.0	9.7	.2	1.14
15	3.0	3.2	.4	1.43
16	11.1	14.3	.2	.96
(7,k,2)				
0	14.0	13.6	.2	1.50
1	28.0	30.3	.3	.84
2	10.0	10.6	.2	.03
3	23.8	23.9	.2	.40
4	12.2	12.8	.2	1.83
5	21.7	22.4	.2	.54
6	21.5	21.7	.3	.09
7	19.4	19.9	.2	.61
8	10.2	10.9	.2	.11
9	6.2	6.4	.3	.67
10	12.2	10.9	.2	1.55
11	12.7	13.6	.2	1.65
12	3.1	3.5*	.4	.32
13	11.8	11.9	.2	1.52
14	15.1	19.0	.2	1.10
15	22.6	14.4	.2	1.54
16	6.3	7.4	.2	1.28
(7,k,3)				
0	27.0	29.2	.3	1.50
1	7.7	7.9	.3	.89
2	7.1	8.3	.3	.24
3	28.8	28.8	.3	.40
4	2.7	6.0*	.4	1.91
5	29.6	30.7	.3	.56
6	13.6	12.8	.2	1.64
7	25.0	25.5	.3	.58
8	13.9	14.5	.2	.30
9	4.5	4.1	.3	.98
10	15.3	15.3	.2	.39
11	3.8	3.8	.3	.68
12	2.1	2.2*	.4	1.46
13	7.8	8.2	.2	1.53
14	6.1	7.3	.2	.91
15	15.1	17.0	.2	1.52
(7,k,4)				
0	16.1	16.7	.2	1.50
1	17.7	17.2	.2	.19
2	7.1	7.5	.3	1.03
3	3.6	2.1	.5	.56
4	12.3	11.1	.2	.44
5	24.7	24.5	.3	.36
6	10.7	10.7	.2	1.00
7	23.2	23.4	.2	.44
8	9.6	9.0	.2	.19
9	8.9	9.6	.2	.92
10	3.1	2.6	.4	.65
11	9.1	9.7	.2	1.35
12	4.5	4.8	.2	.57
13	6.3	6.5	.2	1.38
14	1.1	4.1*	.2	.48
(7,k,5)				
0	18.2	17.4	.2	.50
1	11.1	11.0	.3	1.96
2	12.5	14.4	.2	1.35
3	15.9	17.3	.2	.66
4	12.2	13.1	.2	1.10
5	9.2	8.2	.2	.54
6	11.6	10.4	.2	.56
7	7.8	7.3	.2	.49
8	3.0	3.2	.3	1.40
9	14.8	15.4	.2	.72
10	13.0	12.6	.2	.60
11	2.0	2.5*	.2	.63
12	7.3	8.1	.1	.31
(7,k,6)				
0	2.2	1.2*	.3	.50
1	14.4	14.9	.2	.10
2	10.7	10.8	.2	1.19
3	9.6	9.1	.2	.03
4	11.4	10.9	.2	1.14
5	7.1	7.4	.2	.34
6	14.4	13.3	.2	1.04
7	2.9	2.2	.2	1.30
8	19.6	18.9	.2	.92
9	14.0	12.9	.1	.40
(7,k,7)				
0	2.0	2.6	.3	1.50
1	8.7	9.1	.1	.88
2	6.3	6.2	.1	.86
(8,k,0)				
0	24.0	24.3	.2	1.00
1	10.3	9.8	.2	1.80
2	28.3	28.2	.3	1.00
3	13.3	13.1	.2	.00
4	17.2	17.3	.2	1.00
5	8.4	8.7	.3	.00
6	38.4	38.0	.3	.00
7	2.8	.3*	.4	.00
8	18.1	17.7	.2	.00
9	9.8	8.4	.2	1.00
10	16.2	15.8	.2	.00
11	5.9	6.0	.2	1.00
12	16.2	18.1	.2	.00
13	2.1	.4*	.3	.00
14	9.4	11.5	.2	.00
15	7.3	8.8	.1	1.00
(8,k,1)				
0	22.6	23.7	.2	1.00
1	15.8	17.0	.2	1.67
2	17.9	18.3	.2	1.13
3	25.8	25.3	.3	1.58
4	10.8	10.6	.3	.86
5	14.7	16.7	.2	.19
6	6.3	6.3	.3	1.84
7	4.9	3.6	.4	.46
8	27.2	26.6	.3	1.93
9	3.0	3.4*	.4	.27
10	19.4	18.9	.2	1.84
11	3.7	4.0	.5	.21
12	9.8	10.7	.2	.08
13	3.0	2.9	.3	.84
14	3.6	5.5	.2	.28
15	1.1	1.5*	.2	.94
(8,k,2)				
0	29.2	30.0	.3	1.00
1	19.2	19.9	.2	1.54
2	9.5	9.6	.3	.95
3	14.8	15.4	.2	1.54
4	3.3	3.0*	.4	.00
5	20.4	20.3	.2	.64
6	4.8	4.6	.3	.69
7	12.9	13.0	.2	.30
8	2.9	2.0*	.4	1.35
9	8.8	7.7	.2	.45
10	18.6	18.7	.2	1.93
11	9.9	9.7	.2	.78
12	11.1	11.4	.2	.03
13	8.8	8.9	.2	.60
14	4.8	9.3	.1	.32
(8,k,3)				
0	4.7	6.4	.4	1.00
1	29.6	30.7	.3	1.55
2	7.3	6.9	.3	.67
3	9.6	9.7	.2	1.12
4	4.6	4.9	.3	1.52
5	22.6	20.5	.2	1.44
6	15.5	17.6	.2	1.09
7	8.8	9.7	.2	.47
8	11.3	10.2	.2	1.48
9	26.5	25.9	.2	.49
10	4.1	4.2	.3	.18
11	10.1	9.5	.2	.45
12	7.7	7.8	.2	1.85
13	9.3	9.7	.1	.54
(8,k,4)				
0	20.2	20.2	.2	.00
1	15.5	15.8	.2	1.27
2	5.4	4.0	.2	.05
3	8.6	7.2	.2	1.34
4	4.6	5.6	.3	.73
5	7.6	7.3	.2	.44
6	3.8	4.6	.4	1.12
7	8.3	8.7	.2	.76
8	8.1	7.6	.2	.62
9	20.6	19.9	.2	.65
10	9.0	7.5	.2	.82
11	19.5	19.2	.2	.40
(8,k,5)				
0	26.2	25.9	.2	.00
1	8.8	8.8	.2	1.31
2	2.4	1.5*	.3	1.60
3	15.2	13.9	.2	1.41
4	1.8	1.6*	.3	.41
5	8.7	8.3	.2	1.32
6	6.6	6.6	.2	.05
7	8.1	8.7	.2	.68
8	10.3	10.0	.1	.87
9	10.8	9.1	.1	.53
(8,k,6)				
0	10.7	9.7	.1	.00
1	9.0	10.0	.1	1.82
2	17.6	17.0	.2	1.97
3	7.0	7.4	.1	1.43
4	8.1	7.5	.1	.01
5	1.0	.5*	.2	.54
(9,k,0)				
1	2.6	.1*	.6	1.00
2	5.4	4.7	.3	1.00
3	8.8	8.4	.2	1.00
4	23.8	22.8	.2	1.00
5	16.8	15.5	.2	.00
6	15.2	14.7	.2	1.00
7	6.2	5.2	.3	1.00
8	14.8	15.3	.2	1.00
9	3.6	.9	.3	2.00
10	18.1	18.9	.2	1.00
11	13.2	15.1	.2	.00
12	10.8	11.4	.1	.00
(9,k,1)				
0	13.2	12.7	.2	1.50
1	12.8	13.4	.2	1.67
2	9.1	9.2	.2	.87
3	4.6	4.1	.3	1.39
4	11.2	10.7	.2	1.22
5	2.9	4.5*	.4	1.08
6	16.8	17.2	.2	1.17
7	6.3	6.0	.2	1.56
8	11.5	11.4	.2	.76
9	17.4	17.3	.2	1.84
10	11.1	10.2	.2	.54
11	10.9	11.4	.2	1.57
12	2.5	3.3	.3	1.90
(9,k,2)				
0	11.5	10.5	.2	1.50
1	10.8	10.4	.2	.92
2	17.4	18.0	.2	1.36
3	12.0	11.2	.2	1.46
4	13.2	13.1	.2	1.25
5	6.3	5.9	.2	1.18
6	13.8	12.7	.2	.94
7	9.5	9.6	.2	1.87
8	10.3	10.7	.2	1.04
9	13.6	12.0	.2	1.48
10	8.9	8.0	.2	.44
11	2.2	1.8	.4	.82
(9,k,3)				
0	10.1	8.9	.2	1.50
1	7.8	7.3	.2	1.00
2	4.1	4.0	.3	.96
3	10.1	9.4	.2	1.29
4	10.5	10.8	.2	1.31
5	20.5	19.6	.2	1.50
6	18.4	8.8	.2	.68
7	18.7	16.9	.2	1.55
8	11.0	10.1	.2	.57
9	9.0	8.6	.1	1.57
10	10.2	10.6	.1	.34
(9,k,4)				
0	12.3	11.9	.2	1.50
1	5.4	5.7	.3	.93
2	12.8	13.7	.2	1.53
3	9.3	8.7	.2	1.44
4	3.7	4.3	.2	.52
5	13.9	14.0	.2	1.49
6	5.8	5.7	.2	.27
7	16.4	15.2	.2	1.50
8	9.7	9.5	.1	.15
(9,k,5)				
0	4.5	4.9	.2	1.50
1	14.9	14.0	.1	1.57
2	4.1	3.2	.1	.26
3	6.8	6.2	.1	1.56
4	4.8	4.5	.1	.19
(10,k,0)				
0	2.1	.6*	.3	1.00
1	2.7	1.6	.4	1.00
2	20.1	18.4	.2	.00
3	5.3	4.5	.2	1.00
4	14.1	13.3	.2	.00
5	17.1	14.9	.2	1.00
6	4.8	6.2	.2	.00
7	12.5	11.6	.2	1.00
8	9.6	9.6	.1	1.00
9	8.1	7.7	.1	1.00
(10,k,1)				
0	7.0	6.8	.2	.00
1	6.0	5.8	.3	.38
2	1.6	6.4*	.3	.38
3	13.5	12.9	.2	.90
4	3.2	3.3	.4	1.78
5	12.6	13.1	.2	1.04
6	11.3	10.0	.2	1.22
7	11.1	10.3	.1	1.16
8	4.0	3.6	.2	.79
9	10.2	9.7	.1	1.06
(10,k,2)				
0	9.1	8.5	.2	.00
1	9.0	9.0	.2	.79
2	9.3	9.3	.2	1.96
3	9.4	6.5	.2	.86
4	3.9	4.4	.3	1.01
5	4.6	3.0	.2	.74
6	10.8	11.0	.2	1.70
7	14.8	14.0	.2	1.19
8	10.0	9.6	.1	1.37
(10,k,3)				
0	13.2	12.8	.2	.00
1	15.9	15.1	.2	.60
2	8.2	7.1	.2	1.29
3	8.2	7.8	.2	.65
4	10.4	9.7	.2	1.46
5	3.8	3.3	.2	.94
6	6.2	5.2	.1	1.28
(11,k,0)				
1	17.3	15.0	.2	.00
2	4.7	3.9	.1	1.00
(11,k,1)				
0	3.4	3.5	.2	.50
1	17.2	16.8	.2	.12

Table 3. *Estimated standard deviations*

	Positional parameters	Temperature factors
Ca	0·001 Å	0·04 Å^2
O(1)–O(7)	0·005	0·2
O(*W*1)–O(*W*5)	0·007	0·3
C(1)–C(6)	0·006	0·2
H(1)–H(4)	0·08	2
H(*W*1*a*)–H(*W*5)	0·10	3

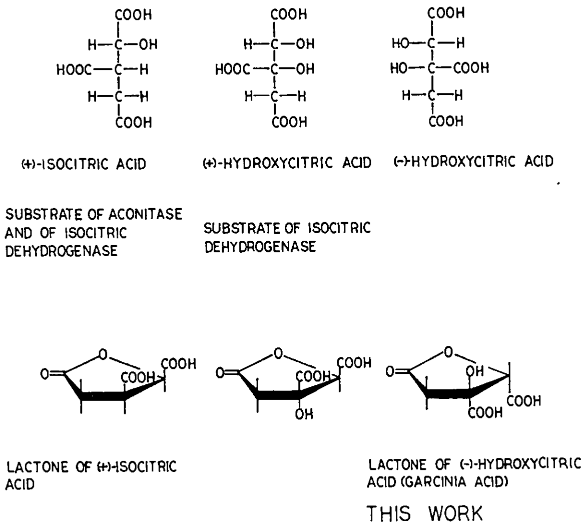
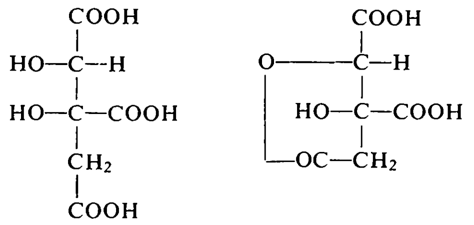


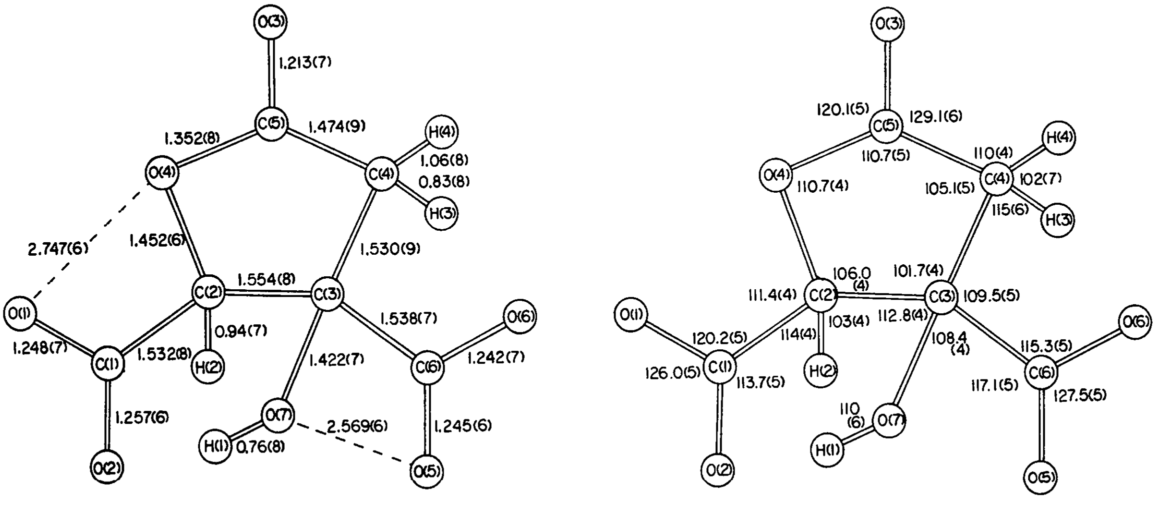
Fig. 1. Absolute configuration of (−)-hydroxycitric acid and related compounds.



Refinement of the structure

To continue the refinement of the structure the data were corrected for anomalous dispersion by Patterson's (1963) method (formula 5). The *R* value dropped to 0·080, at which stage a difference Fourier synthesis was computed and all hydrogen atoms were located. Further least-squares calculations were made with isotropic temperature factors for the hydrogen atoms. The *R* value dropped to 0·058 and to 0·055 after an extinction correction was applied (Zachariasen, 1963*a*) in the form $F_{corr}=F_{obs}\,(1+\alpha\beta_{(2\theta)}\ \mathrm{Lp}\ |F_{obs}|^2)$ with $\alpha=14\cdot5\times10^{-6}$ and values of $\beta_{(2\theta)}$ listed by Zachariasen, (1963*b*). After two cycles of full-matrix least-squares refinement the *R* value dropped to 0·050.

Final parameters of atoms and estimated standard deviations computed from the inverted full-matrix are listed in Table 1. Table 2 lists observed and calculated structure factors together with the computed phase angles and standard deviations of the observed structure factors calculated from counting statistics and measured



C(5)–C(4)–H(3)	115(6)
C(3)–C(4)–H(4)	110(4)
C(4)–C(3)–O(7)	113·5(5)
C(6)–C(3)–C(2)	110·9(4)
C(1)–C(2)–C(3)	114·4
O(4)–C(2)–H(2)	107(4)

Fig. 2. Distances (Å) and angles (°) in the lactone ion. Estimated standard deviations are given in parentheses for the last digit listed. Some additional angles are listed below the figure.

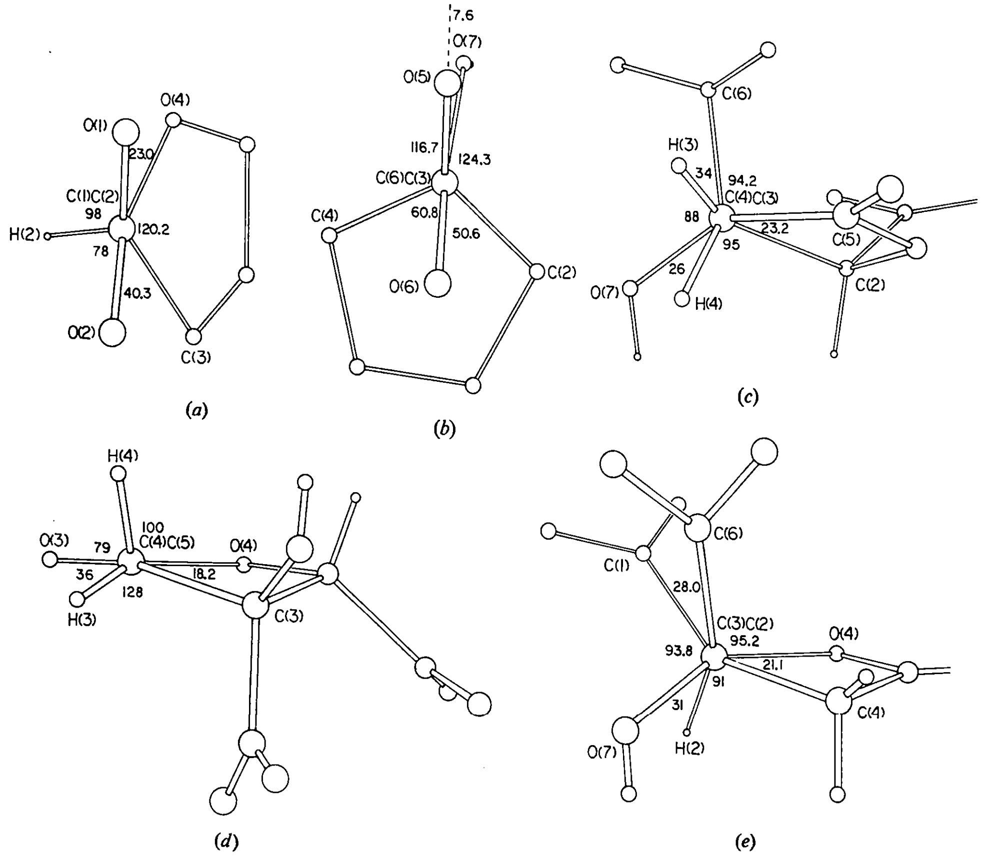


Fig. 3. Some torsion angles, in degrees, given with a view of part or all of the lactone ion with respect to the view down the (*a*) C(1)–C(2), (*b*) C(6)–C(3), (*c*) C(4)–C(3), (*d*) C(4)–C(5) and (*e*) C(3)–C(2) bonds.

Table 4. *Planarity of groups in the lactone ion*

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

(*a*) Carboxyl groups and nearby oxygen atoms

O(1)	−0·007*	O(5)	−0·005*
O(2)	−0·007*	O(6)	−0·005*
C(1)	0·019*	C(6)	0·013*
C(2)	−0·005*	C(3)	−0·004*
O(4)	0·473	O(7)	0·139

(*b*) Lactone ring	O–CO–C	–C–O–CO–C	C–O–C	Whole ring
C(2)	0·082	0·000*	0·026*	−0·073*
C(3)	0·442	0·292	0·399	0·184*
C(4)	−0·002*	−0·103	−0·013*	−0·170*
C(5)	0·008*	0·000*	0·003*	−0·012*
O(3)	−0·003*	0·053	0·017*	0·086*
O(4)	−0·002*	0·000*	−0·033*	−0·015*

(*c*) Polyhedron of oxygen atoms around the calcium ion

O(7)	−0·123*	2·554
O(3)	0·095*	2·588
O(*W*4)	−0·127*	2·366
O(5)	0·155*	2·792
O(*W*1)	−2·811	−0·126*
O(*W*2)	−2·477	0·112*
O(*W*3)	−2·563	−0·112*
O(5′)	−2·438	0·126*
Ca	−1·341	1·231

instrumental uncertainties [determined from standard deviations of the standard reflection and of filter factors (Johnson, 1965*a*)]. The weights, ω, used in the least-squares calculations were proportional to the squares of the inverses of the standard deviations of structure factors. Estimated standard deviations of positional and temperature factor parameters are given in Table 3.

Computations

Most of the computations were performed on an IBM 1620 computer with a 20K memory. Earlier contributions from this laboratory give a listing of programs (Johnson, 1965*a*; Glusker, Van der Helm, Love, Minkin & Patterson, 1968). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Scattering factors for hydrogen were the values given by Stewart, Davidson & Simpson (1965). The quantity minimized in the least-squares calculation is $\sum\omega(|kF_o|-|F_c|)^2$.

In the final stages of refinement (*R* below 0·055) a version of the full-matrix least-squares program *UCLALS*4 of Gantzel, Sparks, Long & Trueblood (1969), which minimizes the same quantity, $\sum\omega(|kF_o|-|F_c|)^2$, was calculated on a UNIVAC 1108 computer (via a DCT 2000 terminal). Interatomic distances, angles, planes and torsion angles were calculated with program *ALLD*, written by A. Caron & H. L. Carrell.

Discussion of the structure

This structure determination shows that in the lactone of (−)-hydroxycitric acid the two carboxyl groups are in positions *cis* with respect to the lactone ring. This configuration was also found for the lactone of (+)-isocitric acid (Glusker, Patterson, Love & Dornberg, 1963). The absolute configuration for this salt is also known (Patterson, Johnson, Van der Helm & Minkin, 1962). Diagrams of both anions are shown in Fig. 1. The lactone of (+)-hydroxycitric acid is included for

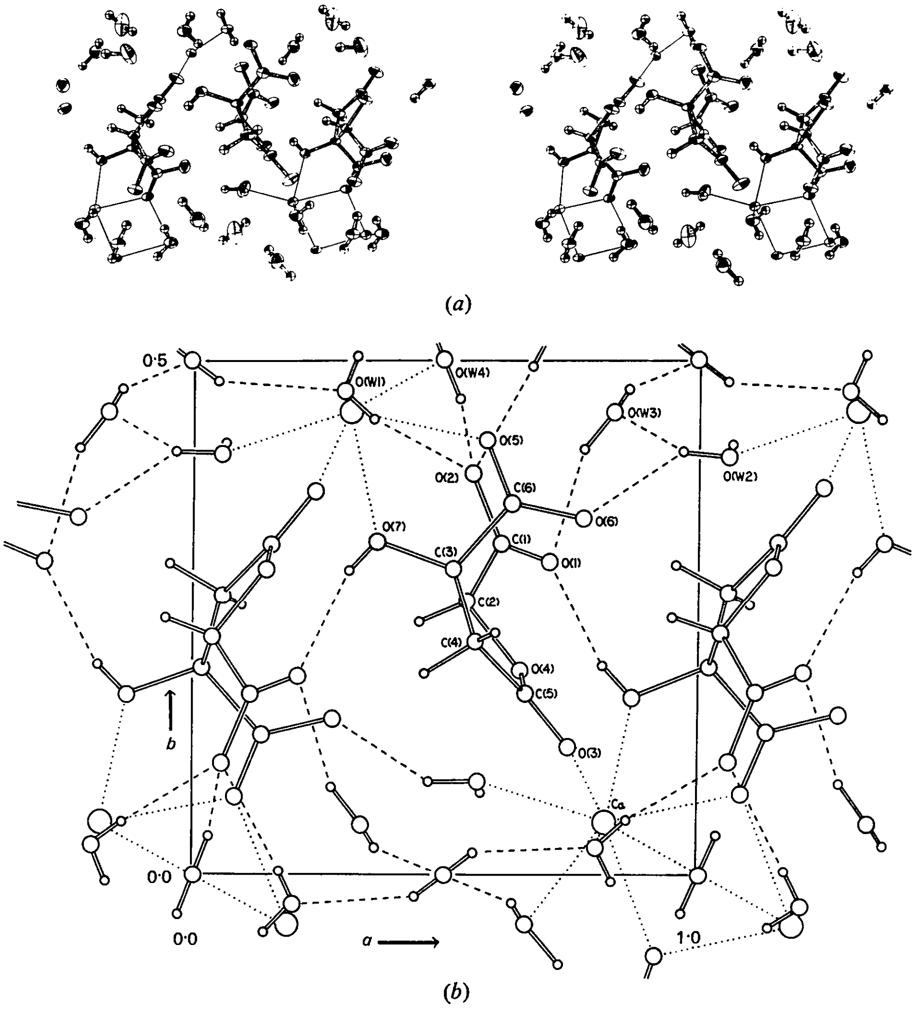


Fig. 4. General packing of the crystal. (*a*) Stereodiagram (Johnson, 1965*b*) and (*b*) line drawing. Hydrogen bonds are indicated by broken lines and calcium–oxygen coordination interactions by dotted lines.

comparison. The structures of the lactones from (+)-hydroxycitric acid and (+)-isocitric acid are identical apart from the additional hydroxyl group in the former. Both of these are substrates of the enzyme isocitric dehydrogenase in the Krebs cycle, and it must be concluded that this hydroxyl group in the substrate molecule is not in a position that is of importance in its interaction with the enzyme.

The distances and angles in the lactone ion are shown in Fig. 2. The estimated standard deviations of bond lengths and angles are given in parentheses. Fig. 2 shows that, from the equality of the four C–O dis-

Table 5. *Hydrogen-bond system*

		Donor (*D*) and acceptor (*A*)				
		D---*A* (Å) (e.s.d. 0·007)	H–*D* (Å) (e.s.d. 0·09)	H---*A* (Å) (e.s.d. 0·09)	∠*A*---H–*D* (°) (e.s.d. 9°)	∠H–*D*---*A* (°) (e.s.d. 7°)
O(*W*4)–H(*W*4) ---O(2)	$-x, -y, z$	2·680	0·82	1·88	163	12
O(7)—H(1) ---O(1)	$x-\frac{1}{2}, \frac{1}{2}-y, -z$	2·698	0·76	1·96	163	12
O(*W*3)–H(*W*3*b*)---O(*W*5)	x, y, z	2·765	0·63	2·17	158	17
O(*W*2)–H(*W*2*a*)---O(6)	x, y, z	2·796	0·84	2·17	131	36
O(*W*5)–H(*W*5) ---O(*W*1)	x, y, z	2·831	0·72	2·21	144	27
O(*W*1)–H(*W*1*b*)---O(2)	$1+x, y, z$	2·884	0·83	2·08	162	13
O(*W*1)–H(*W*1*a*)---O(2)	$1-x, -y, z$	2·899	0·67	2·24	166	11
O(*W*2)–H(*W*2*a*)---O(*W*3)	$1-x, -y, z-1$	2·903	0·84	2·24	135	33
O(*W*3)–H(*W*3*a*)---O(1)	$1-x, -y, z$	3·044	0·90	2·18	159	14

Water angles (e.s.d. values in parentheses)

H(*W*1*a*)–O(*W*1)–H(*W*1*b*)	99°	(12)
H(*W*2*a*)–O(*W*2)–H(*W*2*b*)	105	(21)
H(*W*3*a*)–O(*W*3)–H(*W*3*b*)	111	(10)
H(*W*4)—O(*W*4)–H(*W*4′)	111	(7)
H(*W*5)—O(*W*5)–H(*W*5′)	106	(10)

Table 6. *Coordination around the calcium ion*

(*a*) Distances from the calcium ion (e.s.d. values in parentheses)

Ca---Ca	$-x, -y, z$	3·624 Å
	$-1-x, -y, z$	5·698
Ca	O(5′)	2·392 (4) Å
	O(*W*2)	2·399 (8)
	O(5)	2·419 (4)
	O(7)	2·481 (4)
	O(3″)	2·470 (5)
	O(*W*1)	2·476 (5)
	O(*W*4)	2·492 (4)
	O(*W*3)	2·522 (6)

(*b*) Distances and angles in the polyhedron round the calcium ion

O_A–Ca–O_B, angles (degrees) within the polyhedron (e.s.d. values 0·2°)

	O(*W*4)	O(*W*3)	O(*W*2)	O(*W*1)	O(7)	O(5′)	O(5)
O(3)	78·0	77·7	80·1	148·7	85·0	137·8	106·2
O(5)	65·2	138·0	139·5	84·4	63·2	78·0	
O(5′)	65·6	73·1	124·4	72·7	130·1		
O(7)	117·7	155·8	77·9	73·5			
O(*W*1)	132·1	114·3	73·5				
O(*W*2)	151·5	82·5					
O(*W*3)	75·3						

(*c*) Ca–O---H angles and H–Ca distances

Distances are given in Å and angles in degrees (e.s.d. values in parentheses)

	H–Ca	∠H–O–Ca
H(*W*11)–O(*W*1)–Ca	2·78 (12)	100 (10)
H(*W*12)–O(*W*1)–Ca	2·92 (11)	114 (7)
H(*W*21)–O(*W*2)–Ca	3·12 (11)	143 (7)
H(*W*22)–O(*W*2)–Ca	2·52 (15)	102 (20)
H(*W*31)–O(*W*3)–Ca	2·96 (9)	110 (6)
H(*W*32)–O(*W*3)–Ca	2·74 (10)	104 (8)
H(*W*4)—O(*W*4)–Ca	2·89 (7)	111 (4)
H(*W*5)—O(*W*5)–Ca	2·94 (7)	115 (5)

tances in the carboxyl groups (1·242–1·257 Å), both carboxyl groups are ionized. The bond length C(5)–O(4) is shorter than C(2)–O(4) as found for other lactones (Jeffrey, Rosenstein & Vlasse, 1967), in keeping with the fact that C(5) has a planar configuration about it whereas C(2) has a tetrahedral configuration about it. The extent to which various groupings are planar is given in Table 4. The oxygen atom O(4) lies nearly in the plane of O(1), O(2), C(1), C(2) and the atom O(7) lies nearly in the plane of O(5), O(6), C(6), C(3). The distances of O(1)---O(4) and O(5)---O(7) are 2·747 and 2·569 Å respectively. The approximate planarity of this type of grouping has been found consistently in the citrates and an isocitrate (Glusker, 1968) and has been reported previously in other structures by Jeffrey & Parry (1952). The system -O(4)–C(5)O(3)–C(4)- is also planar (Jeffrey & Kim, 1966); C(2) lies nearly in this plane (0·026 Å from it) while C(3) is 0·399 Å from the plane. In Fig. 3 some torsion angles are illustrated as views of the lactone ion down certain bonds. Other views show the *cis*-configuration of the carboxyl groups and the tendency to staggered conformations down carbon–carbon single bonds.

The environments of each oxygen atom of the lactone ion are interesting. Of those which form hydrogen bonds, O(2) forms three, O(1) forms two and O(6) forms one. Atom O(3) coordinates to one calcium ion and O(5) to two calcium ions. Atom O(7) coordinates to one calcium ion and also forms a hydrogen bond. It might be presumed from these observations that the highest negative charge is found to be on O(5). The chelation of the ion to calcium ions is through O(5) and O(7) to form a five-membered ring: Ca O(7)C(3)C(6)O(5).

The general packing in the crystal, shown in a stereodiagram (Johnson, 1965*b*), Fig. 4(*a*), and by a line drawing in Fig. 4(*b*), is determined both by the packing of oxygen atoms about the calcium ions and by hydrogen bonding of water molecules. The hydrogen-bond system, for which distances are given in Table 5, is illustrated. The surroundings of each carboxyl group and of some water molecules are shown in Fig. 5. The positions of atoms in each diagram

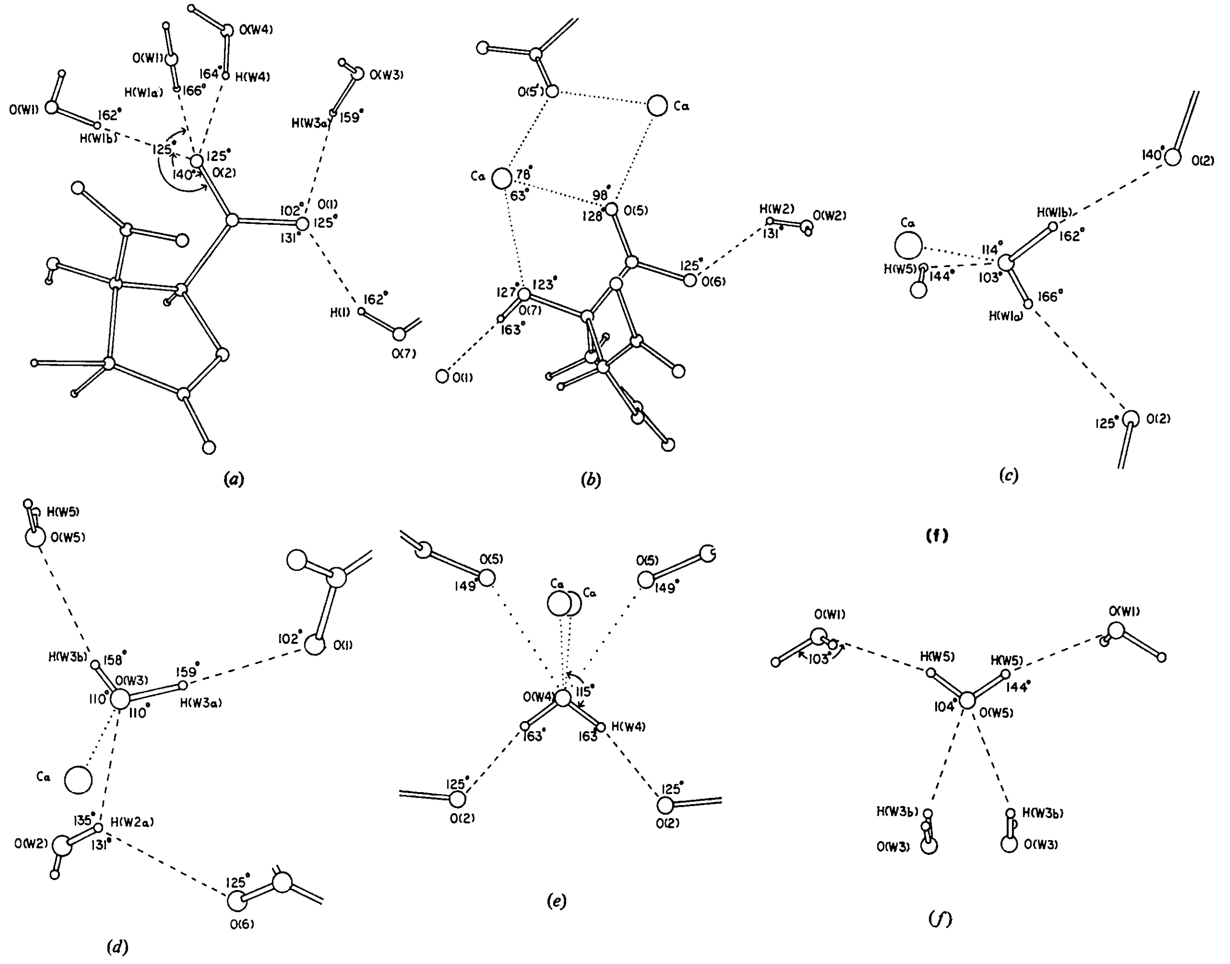


Fig. 5. Packing around carboxyl groups and water molecules. Some angles of interest are shown packing around (*a*) O(1)–O(2)–C(1)–C(2), (*b*) O(5)–O(6)–C(6)–C(3), (*c*) O(*W*1), (*d*) O(*W*3), (*e*) O(*W*4) and (*f*) O(*W*5).

are shown with respect to the plane through the carboxyl groups or water molecules.

The water molecule O(*W*4), which lies on a twofold axis, packs close to the calcium ion and forms a hydrogen bond to O(2) [Fig. 5(*e*)]. It also packs very close to O(5) at 2·65 Å although no hydrogen bond is formed. To check this proximity of oxygen atoms the atom O(*W*4) was moved along the twofold axis but the *R* value increased to 0·067 as *z* was either increased or decreased by 0·018 *c*. The hydrogen atom H(*W*4) is the only large peak on the difference map (calculated with hydrogen-atom contributions omitted from the structure-factor calculation) and its position refined satisfactorily. Based on the data, it is concluded that this short distance, O(*W*4)---O(5), of 2·65 Å is an oxygen–oxygen packing distance, a fact consistent with the observations of Templeton (1960) and Clark (1963) that a hydrogen bond is not formed along the edge of a polyhedron of oxygen atoms around a cation.

The hydrogen atom H(*W*2*b*), located from the difference map, refined by full-matrix least-squares to a position only 0·42 Å from the oxygen atom. However, all other positions chosen for this atom [from lower peaks on the difference maps or from a consideration of possible hydrogen bonding, *e.g.* to O(6) or to O(*W*3)] refined to this position. In these refined positions the hydrogen atom, H(*W*2*a*), is pointing at both O(6) and O(*W*3) [Fig. 5(*d*)] and the hydrogen atom, H(*W*2*b*), is not close to anything. The position of H(*W*2*a*) may, however, be determined by the tendency of the carboxyl group O(5)C(6)O(6) to keep the angle C(6)–O(6)–H(*W*2*a*) near 120° [Fig. 5(*b*)]; hence, there is no way for H(*W*2*b*) to hydrogen-bond as it cannot lie near enough to an oxygen atom without coming too close to the calcium ion. A consideration of the thermal motion of O(*W*2) and O(*W*5) did not clarify the problem. Therefore, the position listed for H(*W*2*b*) which does not correspond to any hydrogen bonding and which may be the average of disordered positions is the best that the data give.

The lactone ions pack in sheets parallel to the *a* axis as shown in Fig. 4(*b*). Such sheets are separated by sheets of calcium ions and water molecules. As seen in Fig. 5(*b*) two calcium ions are coordinated to O(5) in a plane with O(6) and O(7) and O(*W*2). This is also shown in Figure 4(*b*). Below this plane in the crystal is another plane in which O(2) is hydrogen-bonded to O(*W*1) and O(1) is hydrogen-bonded to O(*W*3) and O(7).

The coordination around the calcium ion is described numerically in Tables 4(*c*) and 6 and illustrated in Fig. 6(*a*) and (*b*). Eight oxygen atoms exist at distances 2·391–2·522 Å around the calcium ion. The surroundings are in the form of a distorted square antiprism. The angles and distances in this antiprism are shown in Fig. 6(*b*). This arrangement may also be seen from the planes in Table 4. The edge of the polyhedron containing O(5), O(5′) and O(*W*4) is shared with another calcium ion related by a twofold axis, and the angle between the planes Ca O(5) Ca′ and Ca O(5′) Ca′ is 33°53′.

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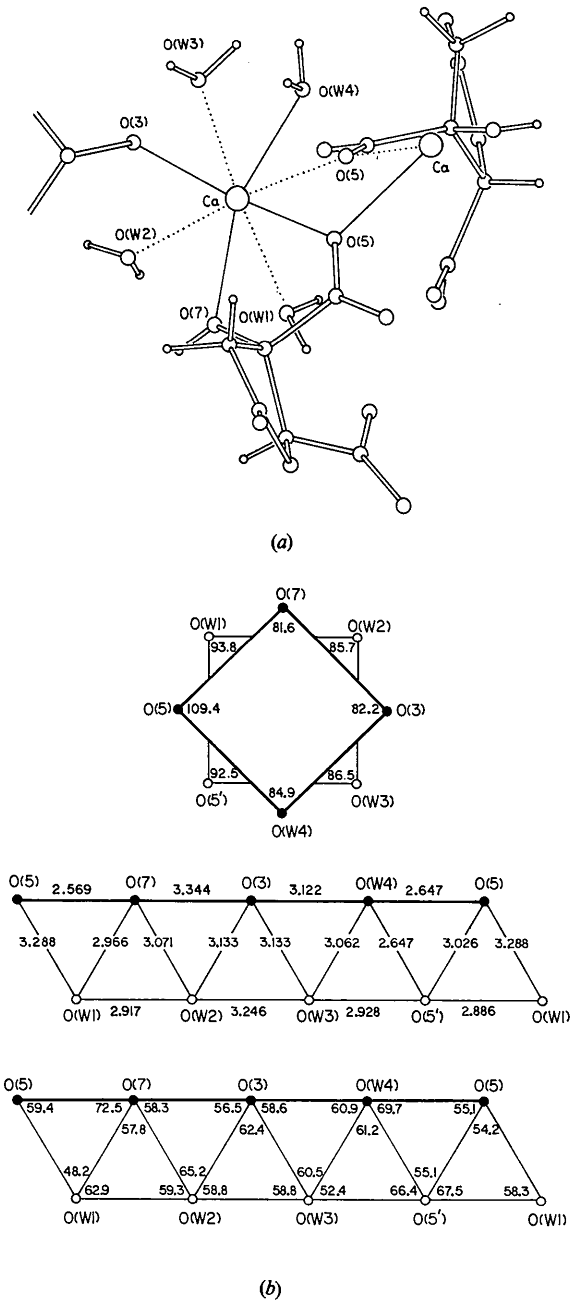

Fig. 6. Packing of oxygen atoms around the calcium ion. (*a*) Packing of lactone ions and water around the calcium ion and (*b*) angles and distances in the square antiprism of calcium coordination.

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The Crystal and Molecular Structure of 4-Methyl Sulfonic Acid (*p*-Toluenesulfonic Acid) Monohydrate, $C_7H_8SO_3^-.H_3O^+$, an Oxonium Salt

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The crystal structure of *p*-toluenesulfonic acid monohydrate has been determined using 1274 three-dimensional intensities measured on a Picker four-circle diffractometer. The crystals are monoclinic, space group $P2_1/c$, with unit-cell dimensions $a=5{\cdot}881$, $b=7{\cdot}431$, $c=20{\cdot}085$ Å, and $\beta=97{\cdot}95°$. The structure was solved by the heavy-atom technique and refined by full-matrix least-squares to an R of 0·04. The structure consists of a pyramidal oxonium ion, H_3O^+, hydrogen bonded to three oxygen atoms of different sulfonate groups. These hydrogen bonds are fairly short, average 2·53 Å. The $S\cdots\bar{O}$ bond distances are equal (average 1·456 Å) within experimental errors. The conformation of the sulfonate group is such that one of the S–O bonds is approximately normal to the ring. This is the preferred conformation for the sulfonate group. The conformation of the methyl group is such that two of its hydrogen atoms make projected angles of about 60° to the benzene plane while the third hydrogen atom is close to the plane.

Introduction

A survey (Sundaralingam, unpublished results) of the crystal structures of substituted benzenoid derivatives revealed that the benzenoid rings do not generally possess hexagonal symmetry with the exception of the fully substituted benzenoid derivatives, *e.g.* C_6Cl_6. The mode of distortion of the aromatic nucleus is dependent on the number of substituents, their relative positions on the ring and their electronic properties, *i.e.* whether they are electron withdrawing or electron releasing. In *para*-substituted derivatives, the aromatic ring possesses a mirror plane through C(1) and C(4)

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