The Crystal Structure of Potassium Glucuronate Dihydrate

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The crystal structure of potassium glucuronate dihydrate has been determined by two-dimensional X-ray crystallographic methods. Most bond lengths and angles are close to expected values; the deviations are believed to be largely due to inaccuracies. The potassium ions are coordinated to eight oxygen atoms at distances 2.76 Å — 2.99 Å. All the oxygen-bonded hydrogen atoms appear to take part in hydrogen bonds.

G lucuronic acid is a compound of considerable biological importance. It occurs in many polysaccharides, and glucuronide formation may play an important part in detoxification and in the absorption of various substances. Notable differences in the behaviour of uronic acids and the corresponding aldohexoses have been observed, *e.g.* in the rate of hydrolysis of the glycosides [4] and in the epimerization reactions.[5,6] It has been suggested that the inductive effect of the carboxyl group has a significant stabilizing effect on the glycosidic linkage.[4] A number of related compounds, such as potassium gluconate [1] and α- and β-glucose,[2,3] have been examined by X-ray crystallographic methods, but no such investigation of uronic acids has been reported.*

EXPERIMENTAL. CRYSTAL DATA

A sample of potassium glucuronate dihydrate, $C_6H_7H_9K \cdot 2H_2O$ was recrystallized from aqueous alcohol and well-developed crystals elongated along the c axis obtained. Weissenberg diagrams were taken about the three crystallographic axes using copper radiation ($\lambda = 1.542$ Å). The crystals are orthorhombic, with $a = 11.26$ Å, $b = 16.53$ Å and $c = 5.54$ Å (all $\pm$ 0.5 %). The systematic absences show that the space group is $P2_12_12_1$. There are four molecules $C_6O_7H_9K \cdot 2H_2O$ per unit cell (calculated density 1.72 g/cm³).

The corresponding rubidium salt was prepared by mixing solutions of glucuronic acid and rubidium hydroxide. It was found to be isomorphous with the potassium salt, having unit cell dimensions $a = 11.26$ Å, 17.05 Å, $c = 5.57$ Å and space group $P2_12_12_1$. A trans-

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* *Note added in proof:* After this paper was submitted to publication the same structure (based on two projections) has been published by G. E. Gurr (*Acta Cryst.* **16** (1963) 690). There are no significant differences between his structure and ours.

formation, probably due to loss of water of crystallization, was observed in the course of the exposure time.

The intensities were measured on integrated Weissenberg diagrams by means of a Hilger Watts photometer and corrected for Lorentz-polarization effects. Small crystals of crossection about 0.1×0.1 mm were used and no correction for absorption applied. In the c projection of the potassium salt 178 reflections were recorded with measurable intensities, in b 67, in a 88, the maximum numbers obtainable by copper radiation being 243, 79, and 113, respectively.

DETERMINATION OF THE STRUCTURE.

The c projection. The position of the metal ion was derived from the Patterson synthesis and the structure solved by the isomorphous replacement method, by comparison of the intensities of the reflections from the potassium and rubidium compounds. The atomic coordinates were refined by Fourier- and difference-syntheses and finally by least squares calculations. The hydrogen atoms were located partly from the difference maps, partly by stereochemical considerations. The analytical approximation of Forsyth and Wells [7] to the atomic scattering factor was used. In Fig. 1 the electron density map is shown
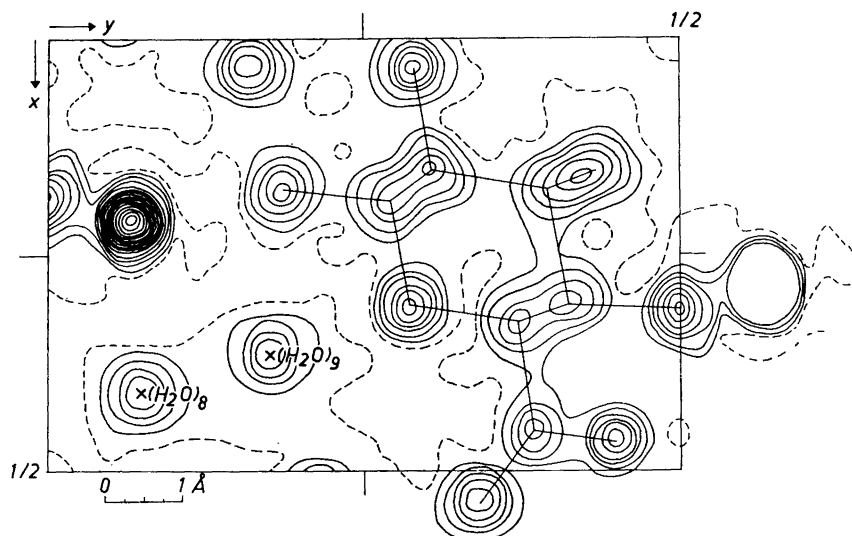

Fig. 1. Electron density projection in direction of c axis. Contours at 1, 3, 5, ... e · Å^{-2}, the first one being broken.

and in Table 3 observed and calculated values of the structure factors are compared. The final value of the reliability index $R = \Sigma ||F_c| - |F_o|| / \Sigma |F_o|$, is 0.07. No correction for extinction was applied. Isotropic temperature factors $\exp(-B\sin^2\Theta/\lambda^2)$ with B between 1.5 and 4.0 were applied to the carbon and most oxygen atoms whereas for the potassium ion and O_4 the anisotropy of the vibrations was taken into account. For both these atoms the direction

Table 1. Atomic coordinates as fractions of the corresponding cell edge.

Atom	x	y	z	B_{hk0}
K	0.2874	0.5651	0.385	2.2 — 1.5
O_1	0.1745	0.1851	0.754	2.6
O_2	0.0344	0.2898	1.072	1.8
O_3	0.1531	0.4342	1.227	2.6
O_4	0.3135	0.5000	0.883	2.5 — 1.0
O_5	0.3105	0.2852	0.694	1.8
O_6	0.4665	0.4496	0.451	2.2
O_7	0.5364	0.3407	0.645	2.2
O_8	0.0900	0.5722	0.692	3.0
O_9	0.1335	0.6767	1.185	4.0
C_1	0.1880	0.2706	0.763	1.5
C_2	0.1545	0.3050	1.001	1.5
C_3	0.1755	0.3968	0.990	1.5
C_4	0.3047	0.4132	0.899	1.5
C_5	0.3285	0.3727	0.661	1.5
C_6	0.4523	0.3875	0.568	1.5

Hydrogen coordinates (assumed)

	x	y	z
H_1	0.138	0.288	0.61
H_2	0.217	0.278	1.15
H_3	0.108	0.413	0.82
H_4	0.382	0.392	1.03
H_5	0.262	0.402	0.52
H_6	0.127	0.173	0.64
H_7	0.037	0.250	1.17
H_8	0.075	0.438	1.20
H_9	0.589	0.520	0.91
H_{10}	0.195	0.605	0.80
H_{11}	0.042	0.622	0.62
H_{12}	0.150	0.713	1.06
H_{13}	0.058	0.700	1.31

of minimum vibration corresponds approximately to the y axis. For all hydrogen atoms $B = 3.0$ was used.

The a projection. Diagrams of the rubidium salt were not available in this zone. The first set of z coordinates were derived from the c projection and approximately known bond lengths and bond angles, considering the possibilities for hydrogen bond formation between molecules. Finally, the potassium ion and the two water molecules were placed so as to obtain reasonable distances from the ion to the surrounding oxygen atoms. The Patterson synthesis did not clearly show the position of the potassium ion. The oxygen atoms O_8 and O_3, as well as O_9 and O_7, overlap badly, and interchange of the z coordinates of these pairs of atoms do not alter the value of R significantly. The z coordinates of O_7 and O_8 were therefore deduced from the b projection, in which they are well resolved. Finally, O_3 and O_9 were located by means of difference syntheses, keeping O_7 and O_8 in fixed positions. The final value of R is 0.09. The values of B are about 0.5 units greater than in the main projection.

Table 2. Interatomic distances (in Å units) and bond angles. Primes indicate atoms in neighbouring molecules.

$C_1 - C_2$	1.48	$O_5 - C_1 - C_2$	115°
$C_2 - C_3$	1.54	$C_1 - C_2 - C_3$	108°
$C_3 - C_4$	1.56	$C_2 - C_3 - C_4$	109°
$C_4 - C_5$	1.50	$C_3 - C_4 - C_5$	112°
$C_5 - C_6$	1.51	$C_4 - C_5 - O_5$	108°
$C_5 - O_5$	1.47	$C_4 - C_5 - C_6$	114°
$O_5 - C_1$	1.45	$O_5 - C_5 - C_6$	108°
$C_1 - O_1$	1.42	$C_5 - C_6 - O_6$	115°
$C_2 - O_2$	1.44	$C_5 - C_6 - O_7$	119°
$C_3 - O_3$	1.47	$O_6 - C_6 - O_7$	125°
$C_4 - O_4$	1.44	$O_5 - C_1 - O_1$	105°
$C_6 - O_6$	1.24	$O_1 - C_1 - C_2$	113°
$C_6 - O_7$	1.28	$C_1 - C_2 - O_2$	115°
$K - O_4$	2.97	$O_2 - C_2 - C_3$	109°
$K - O_4'$	2.99	$C_2 - C_3 - O_3$	111°
$K - O_3'$	2.78	$O_3 - C_3 - C_4$	112°
$K - O_8$	2.80	$C_3 - C_4 - O_4$	105°
$K - O_9$	2.76	$O_4 - C_4 - C_5$	112°
$K - O_1'$	2.84	$C_1 - O_5 - C_5$	109°
$K - O_7$	2.85		
$K - O_6$	2.80		
$O_4 - O_6'$	2.64		
$O_1 - O_7'$	2.73		
$O_2 - O_7''$	2.66		
$O_3 - O_8'$	2.75		
$O_8 - O_2'$	2.76		
$O_8 - O_4$	2.98		
$O_9' - O_2$	2.91		
$O_9' - O_5$	2.82		

The b projection was also refined (to $R = 0.11$) in order to obtain more reliable z coordinates for some of the atoms (O_7 and O_8) which are poorly resolved in the a projection.
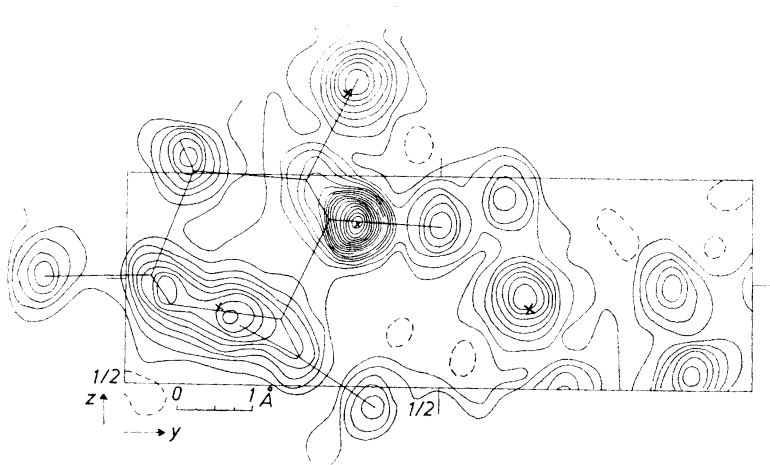
Fig. 2. Electron density projection in direction of a axis. Contours as in Fig. 1.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE.

In Table 1 the final atomic coordinates are given. The x and y coordinates are derived from the c projection, the z coordinates of O_7 and O_8 from the b projection, of the other atoms from the a projection. The corresponding bond lengths and bond angles are collected in Table 2 and Fig. 4. The Cruickshank
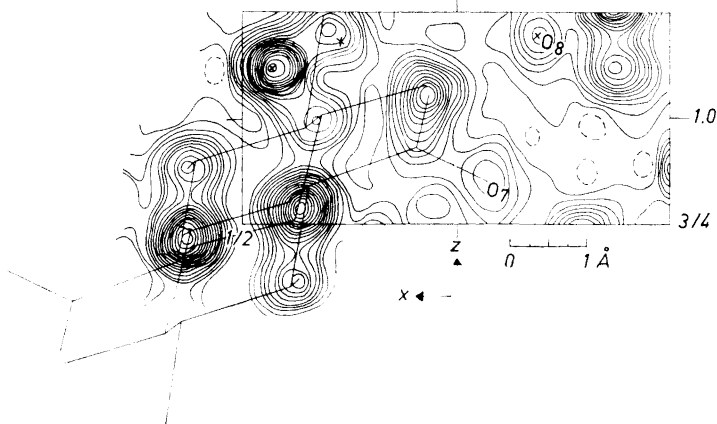

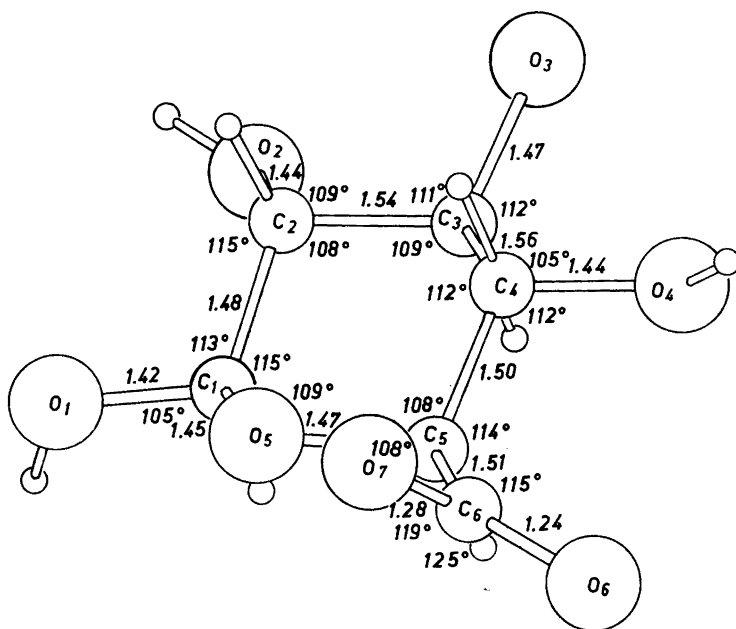*Fig. 3.* Electron density projection in direction of b axis Contours as in Fig. 1.

Fig. 4. The structure of the glucuronate ion.

Table 3. Observed (F_o) and calculated (F_c) structure factors for K glucuronate.

h k l	F_o	F_c	h k l	F_o	F_c
0 2 0	13	8	3 5 0	28	− 30
0 4 0	15	− 17	3 6 0	30	26
0 6 0	50	− 55	3 7 0	10	10
0 8 0	87	−100	3 8 0	< 6	5
0 10 0	18	16	3 9 0	31	− 29
0 12 0	7	6	3 10 0	< 5	3
0 14 0	41	40	3 11 0	7	− 7
0 16 0	33	30	3 12 0	14	− 13
0 18 0	24	27	3 13 0	15	− 15
0 20 0	< 5	1	3 14 0	30	− 30
0 1 0	33	36	3 15 0	35	− 35
1 2 0	14	14	3 16 0	< 8	0
1 3 0	17	17	3 17 0	< 7	0
1 4 0	23	− 21	3 18 0	9	8
1 5 0	17	− 17	3 19 0	< 6	2
1 6 0	22	− 22	3 20 0	12	14
1 7 0	51	54	4 0 0	9	− 2
1 8 0	57	− 56	4 1 0	20	22
1 9 0	13	− 14	4 2 0	18	19
1 10 0	67	67	4 3 0	77	80
1 11 0	7	− 9	4 4 0	12	11
1 12 0	15	15	4 5 0	66	66
1 13 0	< 7	2	4 6 0	19	− 21
1 14 0	13	12	4 7 0	14	14
1 15 0	< 8	5	4 8 0	< 6	1
1 16 0	< 8	2	4 9 0	26	− 27
1 17 0	12	12	4 10 0	20	− 20
1 18 0	22	− 22	4 11 0	32	− 29
1 19 0	6	8	4 12 0	8	− 8
1 20 0	11	− 11	4 13 0	8	− 9
1 21 0	< 4	2	4 14 0	13	13
2 0 0	74	− 84	4 15 0	33	− 30
2 1 0	24	− 25	4 16 0	< 7	4
2 2 0	29	− 27	4 17 0	15	13
2 3 0	19	16	4 18 0	13	12
2 4 0	18	− 19	4 19 0	14	16
2 5 0	29	− 27	4 20 0	< 4	3
2 6 0	36	37	5 1 0	95	100
2 7 0	24	− 24	5 2 0	26	− 26
2 8 0	18	19	5 3 0	9	10
2 9 0	22	18	5 4 0	29	− 32
2 10 0	19	− 17	5 5 0	6	− 3
2 11 0	14	14	5 6 0	8	9
2 12 0	19	− 19	5 7 0	34	− 34
2 13 0	< 7	5	5 8 0	< 7	6
2 14 0	25	− 24	5 9 0	36	− 37
2 15 0	< 6	4	5 10 0	13	13
2 16 0	24	− 25	5 11 0	13	11
2 17 0	6	− 5	5 12 0	25	24
2 18 0	< 7	3	5 13 0	24	22
2 19 0	< 6	3	5 14 0	< 8	4
2 20 0	9	8	5 15 0	32	33
3 1 0	10	− 12	5 16 0	12	− 11
3 2 0	7	8	5 17 0	15	15
3 3 0	26	− 22	5 18 0	< 6	− 8
3 4 0	50	43	5 19 0	< 5	2

h k l	F_o	F_c	h k l	F_o	F_c
6 0 0	80	81	9 3 0	14	15
6 1 0	33	— 33	9 4 0	34	31
6 2 0	29	— 27	9 5 0	11	— 11
6 3 0	< 5	1	9 6 0	22	22
6 4 0	12	9	9 7 0	34	— 34
6 5 0	< 6	0	9 8 0	< 8	2
6 6 0	19	18	9 9 0	13	— 13
6 7 0	23	— 22	9 10 0	14	— 14
6 8 0	< 7	0	9 11 0	< 7	3
6 9 0	12	12	9 12 0	7	— 8
6 10 0	24	23	9 13 0	7	10
6 11 0	33	32	9 14 0	23	— 25
6 12 0	< 8	6	9 15 0	9	10
6 13 0	< 8	8	9 16 0	6	6
6 14 0	< 7	0	10 0 0	< 8	7
6 15 0	< 7	5	10 1 0	8	— 7
6 16 0	< 7	4	10 2 0	17	15
6 17 0	< 6	— 7	10 3 0	9	— 10
6 18 0	< 5	4	10 4 0	13	12
6 19 0	13	— 16	10 5 0	< 8	8
7 1 0	51	— 50	10 6 0	18	— 20
7 2 0	42	40	10 7 0	< 8	2
7 3 0	< 6	1	10 8 0	< 8	3
7 4 0	22	21	10 9 0	< 7	3
7 5 0	< 7	4	10 10 0	< 7	2
7 6 0	22	22	10 11 0	9	11
7 7 0	37	35	10 12 0	13	13
7 8 0	39	39	10 13 0	16	19
7 9 0	20	19	10 14 0	16	17
7 10 0	23	23	10 15 0	14	— 12
7 11 0	< 8	7	11 1 0	10	— 9
7 12 0	8	— 6	11 2 0	15	— 16
7 13 0	8	— 9	11 3 0	< 8	8
7 14 0	8	— 8	11 4 0	17	— 16
7 15 0	21	— 21	11 5 0	27	27
7 16 0	< 6	1	11 6 0	< 6	2
7 17 0	10	— 11	11 7 0	7	7
7 18 0	< 4	3	11 8 0	9	— 6
8 0 0	61	— 64	11 9 0	13	13
8 1 0	22	— 19	11 10 0	13	14
8 2 0	< 6	3	11 11 0	8	9
8 3 0	28	29	11 12 0	8	8
8 4 0	< 6	4	11 13 0	< 4	4
8 5 0	21	19	12 0 0	19	— 19
8 6 0	15	15	12 1 0	< 6	2
8 7 0	< 8	3	12 2 0	7	— 7
8 8 0	< 8	7	12 3 0	13	14
8 9 0	18	16	12 4 0	< 6	2
8 10 0	15	— 16	12 5 0	13	13
8 11 0	13	— 13	12 6 0	7	9
8 12 0	< 7	0	12 7 0	< 6	5
8 13 0	14	— 14	12 8 0	12	13
8 14 0	13	— 11	12 9 0	6	— 8
8 15 0	13	— 15	12 10 0	10	11
8 16 0	< 5	3	12 11 0	6	— 6
8 17 0	4	5	13 1 0	21	— 18
9 1 0	10	10	13 2 0	12	13
9 2 0	10	9	13 3 0	< 6	1

h	k	l	F_o	F_c	h	k	l	F_o	F_c
13	4	0	12	12	0	8	2	15	18
13	5	0	< 5	1	0	8	3	< 5	1
13	6	0	7	7	0	8	4	< 5	1
13	7	0	< 5	2	0	8	5	10	− 9
13	8	0	< 4	3	0	8	6	4	5
13	9	0	7	5	0	9	1	50	− 51
14	0	0	13	− 12	0	9	2	17	21
14	1	0	8	− 7	0	9	3	< 5	6
14	2	0	10	12	0	9	4	19	21
14	3	0	< 4	1	0	9	5	< 5	6
14	4	0	< 4	0	0	9	6	< 4	3
14	5	0	< 3	2	0	10	1	21	− 12
0	0	2	36	− 34	0	10	2	15	− 15
0	0	4	12	− 13	0	10	3	36	41
0	0	6	7	− 5	0	10	4	14	− 13
0	1	1	33	30	0	10	5	13	− 14
0	1	2	34	− 33	0	10	6	< 3	3
0	1	3	34	32	0	11	1	10	10
0	1	4	34	− 35	0	11	2	11	11
0	1	5	< 6	− 7	0	11	3	26	− 31
0	1	6	17	17	0	11	4	< 6	1
0	2	1	52	− 49	0	11	5	10	− 13
0	2	2	32	− 35	0	11	6	< 3	4
0	2	3	48	− 47	0	12	1	23	− 22
0	2	4	33	31	0	12	2	14	− 15
0	2	5	22	23	0	12	3	< 6	4
0	2	6	< 6	6	0	12	4	14	− 15
0	3	1	25	− 25	0	12	5	9	9
0	3	2	99	104	0	13	1	15	− 15
0	3	3	42	46	0	13	2	25	− 23
0	3	4	< 6	3	0	13	3	14	12
0	3	5	6	6	0	13	4	9	− 9
0	3	6	< 6	4	0	13	5	11	11
0	4	1	38	− 36	0	14	1	14	− 11
0	4	2	6	− 10	0	14	2	10	8
0	4	3	53	51	0	14	3	6	11
0	4	4	9	7	0	14	4	18	20
0	4	5	< 6	2	0	14	5	9	− 11
0	4	6	6	− 7	0	15	1	13	− 9
0	5	1	51	59	0	15	2	24	25
0	5	2	29	27	0	15	3	9	3
0	5	3	56	− 58	0	15	4	8	8
0	5	4	< 5	3	0	16	1	< 6	5
0	5	5	10	− 11	0	16	2	6	1
0	5	6	< 5	3	0	16	3	5	7
0	6	1	12	12	0	16	4	10	11
0	6	2	8	9	0	17	1	18	17
0	6	3	7	8	0	17	2	14	18
0	6	4	< 5	2	0	17	3	10	10
0	6	5	13	15	0	18	1	< 5	8
0	6	6	11	− 11	0	18	2	< 4	2
0	7	1	12	12	0	18	3	16	16
0	7	2	25	− 22	0	19	1	< 4	3
0	7	3	< 5	2	0	19	2	< 4	2
0	7	4	13	− 13	0	19	3	7	9
0	7	5	6	6	0	20	1	10	13
0	7	6	15	15	0	20	2	14	15
0	8	1	8	− 7	1	0	1	38	36

h	k	l	F_o	F_c		h	k	l	F_o	F_c
1	0	2	33	36		6	0	6	4	2
1	0	3	33	33		7	0	1	16	21
1	0	4	13	11		7	0	2	25	− 27
1	0	5	14	8		7	0	3	15	14
1	0	6	< 5	3		7	0	4	11	9
2	0	1	69	73		7	0	5	< 5	1
2	0	2	43	44		7	0	6	17	17
2	0	3	< 8	1		8	0	1	20	15
2	0	4	11	10		8	0	2	10	− 6
2	0	5	19	14		8	0	3	20	− 18
2	0	6	< 5	2		8	0	4	< 6	4
3	0	1	10	17		8	0	5	19	19
3	0	2	54	46		9	0	1	43	43
3	0	3	12	11		9	0	2	27	− 28
3	0	4	< 5	2		9	0	3	9	7
3	0	5	11	− 8		9	0	4	< 5	− 3
3	0	6	21	20		9	0	5	9	6
4	0	1	19	− 22		10	0	1	16	− 14
4	0	2	41	− 43		10	0	2	12	− 12
4	0	3	45	− 43		10	0	3	< 5	− 4
4	0	4	27	− 31		10	0	4	12	14
4	0	5	25	− 23		10	0	5	12	17
4	0	6	11	11		11	0	1	8	− 8
5	0	1	30	31		11	0	2	6	− 8
5	0	2	31	− 29		11	0	3	16	17
5	0	3	25	− 28		11	0	4	4	− 4
5	0	4	35	37		12	0	1	8	7
5	0	5	6	− 5		12	0	2	12	9
5	0	6	16	22		12	0	3	7	− 3
6	0	1	40	− 40		13	0	1	18	− 20
6	0	2	9	− 11		13	0	2	< 4	− 1
6	0	3	6	2		13	0	3	< 3	1
6	0	4	19	− 16		14	0	1	< 3	3
6	0	5	9	10						

formulae [5] give the following values for the standard deviations in the atomic coordinates:

$\sigma(x) = \sigma(y) = 0.009$ Å, $\sigma(z) = 0.014$ Å for the carbon atoms;
$\sigma(x) = \sigma(y) = 0.007$ Å, $\sigma(z) = 0.011$ Å for the oxygen atoms;

$0.001-0.002$ Å for the potassium ion in all directions. The corresponding standard deviations lie in the range $0.012-0.019$ Å for the C−C bonds and $0.010-0.015$ Å for the C−O bonds. The lower limit applies to bonds approximately parallel to the xy plane, the upper limit to those roughly perpendicular to this plane. Taking the lack of resolution into account we do not consider discrepancies less than 0.05 Å significant. The standard deviations in the angles probably lie in the range $1-2°$.

The glucuronate ion. As expected, the sugar occurs in its pyranose chair form with all hydroxyl groups, as well as the carboxyl group, in equatorial positions. The interatomic distances are in general close to the expected values of 1.53 Å for C−C bonds and 1.43 Å for C−O bonds. The largest deviation occurs in the C_1-C_2 bond, which is found to be only 1.48 Å. However,

the length of this bond depends mainly on the z coordinates, which are inaccurate because of lack of resolution. We therefore do not believe that the bond really is so short. On the other hand the C_1-O_1 linkage, which has been reported to be unusually short in certain sugars,[3],[13] is found to be of normal length. The angle at the ring oxygen atom is 109°, significantly smaller than found in cellobiose [9] (116°) and a number of other sugars. On the whole, however, the structure determination is not accurate enough to decide whether the deviations in bond lengths and angles are due to errors, or are effects of introducing the carboxyl group.

In compounds containing the groups C(OH)COOH or C(OH)COO⁻ it has been observed that the C—OH bond lies in the plane of the carboxyl group, or nearly so, the distance between carboxyl and hydroxyl oxygen atoms being significantly shorter (2.65 Å) than normal van der Waals separation.[10] In the present case, where the ring oxygen atom takes the place of the hydroxyl group, the effect is less pronounced, the angle between the planes $C_5C_6O_5$ and $C_5C_6O_7$ being roughly 30° and the distance O_5-O_7 2.72 Å.

The atom C_5 and the three atoms of the carboxyl group are planar within the limits of error. The dimensions of the carboxyl group agree with those found in similar compounds.[12]
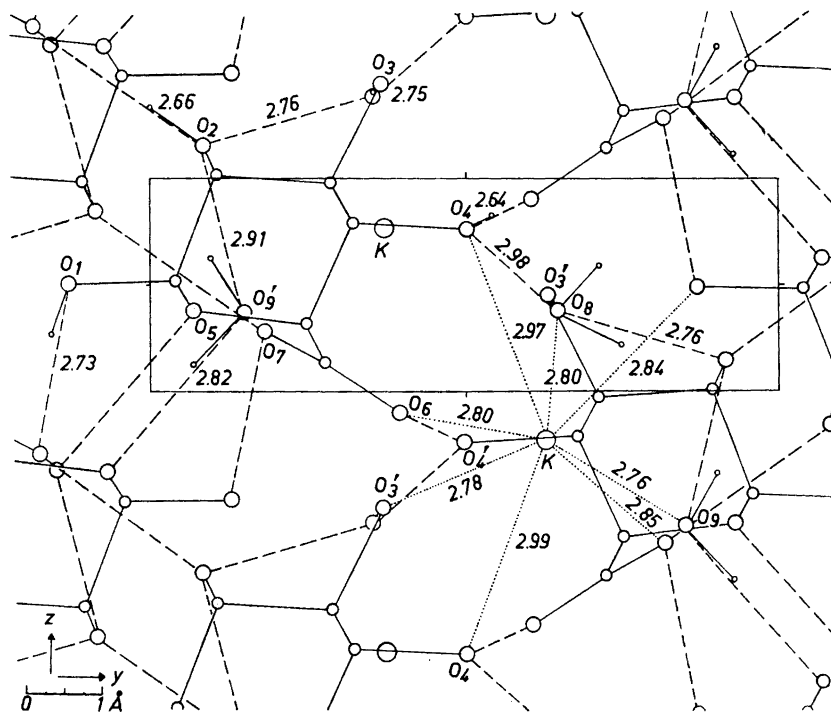

Fig. 5. The structure projected in direction of a axis. Short O—O contacts are shown by broken lines, K—O contacts by dotted lines. The smallest circles indicate the proposed positions of the oxygen-bonded hydrogen atoms.

The ionic environment. Each potassium ion is surrounded by eight oxygen atoms at distances 2.76 Å—2.99, lying in the corners of a distorted Archimedian antiprism. One of the oxygen atoms (O_4) is coordinated to two potassium ions. Each potassium ion is linked to four glucuronate ions. Similar eightfold co-ordinates has been observed in a number of other crystal structures, *e.g.* in potassium ethyl sulphate,[11] where the distances range from 2.80 Å to 3.02 Å.

The hydrogen bonds. The glucuronate ions and the water molecules are linked together in the crystal by a system of hydrogen bonds, as may be inferred from the observed intermolecular oxygen-oxygen distances. There are eight oxygen-bonded hydrogen atoms per asymmetric unit and there are also eight different oxygen-oxygen contacts shorter than 3.0 Å (2.64 Å—2.98 Å). It appears reasonable to assume that these correspond to hydrogen bonds. They are shown by broken lines in Fig. 5. The allocation of hydrogen atoms to the bonds seem fairly evident, as four of the bonds occur between oxygen atoms and hydroxyl groups. The final difference map in the *c* projection lends additional support. The water molecule $(H_2O)_8$ and the hydroxyl group $(OH)_2$ are engaged in three hydrogen bonds, $(H_2O)_9$ and $(OH)_4$ in two, $(OH)_1$ and $(OH)_3$ in only one. The angle between the two hydrogen bonds from the water oxygen atom is 125° at O_9, and as much as 147° at O_8. Consequently, at least one of the hydrogen atoms at O_8 must lie far off the $O_8...O$ directions. We have placed H_{10}, which is engaged in the longest hydrogen bond (2.98 Å) in the structure, in such a position, but the refinement of the structure is not carried so far that other possibilities can be excluded. Apparently, there are no hydrogen bonds between the water molecules, their separations being 3.27 Å and 3.33 Å. The three shortest hydrogen bonds are those involving the carboxyl oxygen atoms (2.64 Å, 2.66 Å and 2.73 Å).

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