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The Crystal Structure of β -D-Glucurono- γ -lactone

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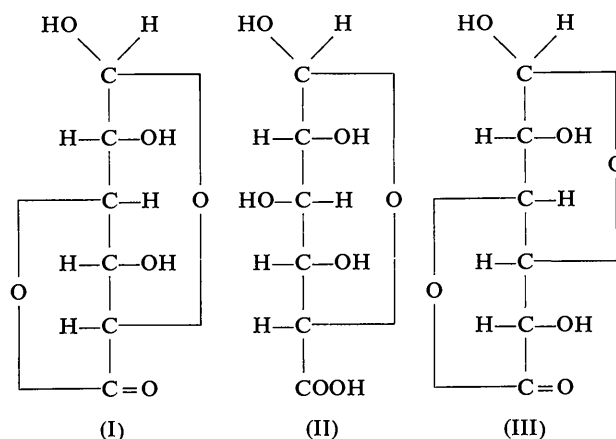
The crystal structure of β -D-glucurono- γ -lactone, $C_6H_8O_6$, has two molecules in a cell with $a=6.753$, $b=7.488$, $c=6.608$ Å, $\beta=93.18^\circ$, space group $P2_1$. The structure was solved from the three-dimensional sharpened Patterson function using multiple minimum function and convolution methods on an IBM 1620 computer. Both photographic and automatic diffractometer data were measured. The former gave a terminal R index of 10% and the latter 4%. The molecule was found to have fused five-membered lactone and furanose rings, in agreement with an earlier deduction from chemical evidence. The rings, neither of which is planar, are inclined to each other so that the best planes containing four atoms in each make a dihedral angle of 111.3° . The lactone group is not planar, having a carbon atom 0.26 Å

out of the plane of the C-C-O group, which is planar. The C-O bond adjacent to the carbonyl group is 0.10 Å shorter than the other formal single C-O bonds in the molecule. The molecules are associated in the crystal by a very simple system of hydrogen bonding, which excludes one hydroxyl group and the ring oxygen atoms.

Introduction

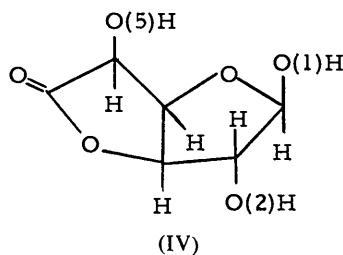
Glucurono- γ -lactone (also called glucurone or glycurone) is of biochemical interest. It is converted into L-ascorbic acid in animals (Chatterjee, Chatterjee, Ghosh, Ghosh & Guha, 1960) and in the human body (Baker, Bierman & Plough, 1960), and has been shown to have an antihypnotic action against sodium 5,5-diethylbarbiturate (Tamura, Tsutsumi & Kizu, 1962). The molecule was originally believed to contain a six-membered pyranose and a five-membered lactone ring as shown in (I), since it is derived from glucuronic acid, which has the pyranose structure (II) like the anion in potassium glucuronate (Gurr, 1963; Furberg, Hammer & Mostad, 1963). However, on the basis of chemical experiments with trimethylglucurono-lactone by Reeves (1940) and Smith (1944), Smith proposed the structure (III) containing two five-membered rings, which is confirmed by this structure determination.

Of the eight stereo-isomers that can be formed by different configurations of the secondary alcohol groups at the three positions in this lactone/furanose ring system, only two can be derived from glucuronic



acid by ring closure without inversion. These two configurations are $1n2x5n$ and $1x2x5n$, where *endo*, n , and *exo*, x , refer to substituents directed towards and away, respectively, from the dihedral angle between the two rings. The β form (IV), which has been found in the crystals studied, is the former conformation, with two *endo* substituents; this is contrary to a rule that the stable derivatives of two fused five-membered ring

compounds are those with the minimum number of *endo* substituents (*cf.* Guthrie & Honeyman, 1964).



These crystals were also found to be identical with those prepared from a sample of calcium 1,2-*O*-isopropylidene- α -D-glucopyranoside, presumably the α form, since it was obtained by oxidation of 1,2-*O*-isopropylidene- α -D-glucopyranose, which requires the $1 \times 2 \times 5n$ configuration (Mehlretter, 1963). Mutarotation therefore takes place at some stage in this preparation of the crystalline glucuronolactone.

The other three of the four possible pairs of γ -lactone/furanose stereoisomers are the α and β anomers of manuronolactone, iduronolactone and guluronolactone, respectively.

Crystal data

Large, transparent crystals were obtained by slow evaporation of an aqueous solution of the compound supplied by Eastman Chemicals. The cell parameters were measured with Cu $K\alpha_1$ radiation using a Picker 4-angle automatic diffractometer. The crystal density was measured at 23°C by the flotation method in a mixture of carbon tetrachloride and bromoform.

D-Glucurono- γ -lactone, $C_6H_8O_6$; M.W. 176.12

Monoclinic, space group $P2_1$, from systematic absences $0k0$ absent for k odd.

$$a = 6.753 \pm 0.006 \text{ \AA}$$

$$b = 7.488 \pm 0.008$$

$$c = 6.608 \pm 0.006$$

$$\beta = 93.18 \pm 0.03^\circ$$

$$Z = 2$$

$$D_m = 1.760 \pm 0.007, D_x = 1.753 \text{ g.cm}^{-3}$$

$$\mu_{Cu K\alpha} = 14.38 \text{ cm}^{-1}$$

The cell parameters reported by Keihn & King (1951) were $a = 6.81$, $b = 7.50$, $c = 6.64 \text{ \AA}$, $\beta = 93.72^\circ$.

Experimental

Two sets of data were collected, one by the photographic method and a second by automatic diffractometer. The photographic data were recorded on multiple film equi-inclination Weissenberg photographs with Cu $K\alpha$ radiation. Four layers were photographed about the a and five layers about the b axis, with average exposure times of 21 hours per layer. The mean diameters of the approximately cylindrical crystals used were 0.3 and 0.5 mm for the a and b axes respec-

tively. Of 832 accessible reflections unrelated by symmetry, 85% were observed above the background of the film, and these were estimated visually by comparison with a standard scale. All intensities were corrected for absorption by linear interpolation of correction factors for cylindrical crystals. The b -axis data were also corrected for the focusing effect of the diffracted beam due to the wide collimator used in taking the data, as described by Buerger (1942). These data were then correlated and reduced to the structure factors using a series of IBM 1620 programs which incorporated the least-squares method of interlayer scaling of Rollett & Sparks (1960).

After the structure was solved, a Picker 4-angle automatic diffractometer became available and a second set of data was collected on a triangular prismatic crystal of base dimensions $0.3 \times 0.3 \times 0.2 \text{ mm}$ and height 0.5 mm. The $\theta/2\theta$ scanning mode was used to measure 578 reflections with 2θ values below 130° in approximately 22 hours, with a 2° scan across each peak and background measurements at both ends. An R value of 3.5% was obtained between 406 duplicate reflections which were measured in two different quadrants of the reciprocal lattice. No absorption corrections were included in reducing these data to structure amplitudes.

Determination of the structure

The structure was determined from the three-dimensional E^2 Patterson function by a superposition procedure on an IBM 1620 computer, using programs prepared by Corfield (1965). Two independent atoms were first located by the recognition of their vector set, using a method related to that described by Alden, Stout, Kraut & High (1964). A sharp peak in a general position was selected as the vector mn [Fig. 1(a)] and the vectors mn' (coincident with nm' by the mirror symmetry) and the Harker peaks mm' and nn' were identified by inspection of the Patterson function. The Patterson function can be inspected in a systematic manner by calculating the multiple minimum function

Table 1. Interpretation of the Patterson function. Results of (a) the minimum function based on three atoms and their symmetry relations, (b) the convolution of the function with the sharpened Patterson function

Relative height of peaks	Number of peaks	
	Atoms	Spurious
(a)		
2	2	—
1	7	1
0	3	22
-1		many
.		.
.		.
.		.
(b)		
> 45	3	
41-45	3	
36-40	5	
31-35	1	3
26-30		5

at $v=0.5$, with vector shifts $(0,0,0)$, (u_{mn}, v_{mn}, w_{mn}) , $(2u_{mn}, 0, 2w_{mn})$ [Fig. 1(b)]. With an arbitrary value for y_m , the coordinates of two atoms were obtained,

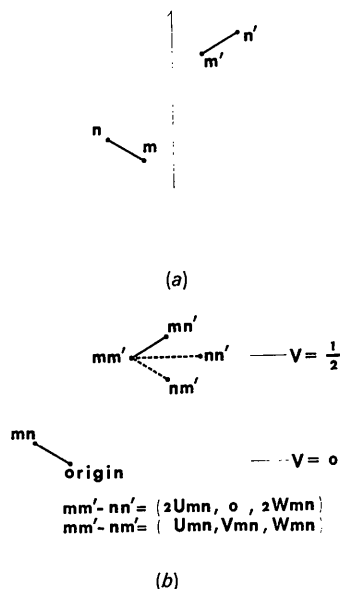


Fig. 1. Two independent atoms in the space group $P2_1$ and their corresponding Patterson vectors. (a) The fundamental set. (b) The vector set (in part).

which proved to be O(2) and C(2) in the ensuing analysis. From these two atomic positions an M_4 multiple minimum function was calculated (Buerger, 1959). Although this could not be interpreted in terms of molecular models, a third atom, O(3), was revealed which permitted the calculation of an M_6 function. This contained peaks corresponding to all the atoms in the structure with a background of additional peaks such that the structure was not recognized. This M_6 function was therefore convoluted with the original sharpened Patterson function by finite integration to emphasize the atomic peaks. The result is compared with the M_6 function in Table 1. There were fewer peaks to take into account, and the structure could now be recognized by correspondence of the highest peaks with a molecular model. The first structure factor calculation gave an R value of 0.28 for all observed reflections.

The motive for using this convolution has been discussed previously, for example, by Ramachandran & Raman (1959), Raman & Lipscomb (1961) and Sax (1963). However, instead of using Fourier methods, the function was computed on the IBM 1620 by generalizing the superposition program and including in the summation only positive values of the two functions, thereby imposing a non-negative criterion, the importance of which has been discussed by Karle & Hauptman (1963).

Table 2. Fractional atomic coordinates in β -D-glucurono- γ -lactone

(For atomic numbering see Fig. 2)

The estimated standard deviations in parentheses refer to the last decimal positions of respective values.

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
C(1)	0.2122 (6)	0.0819 (6)	0.4143 (5)	H(C1)	0.21	-0.01	0.51
C(2)	0.0080 (5)	0.1375 (6)	0.3281 (5)	H(C2)	-0.08	0.205	0.44
C(3)	0.0587 (5)	0.2606 (7)	0.1557 (5)	H(C3)	-0.04	0.293	0.02
C(4)	0.2616 (5)	0.1959 (7)	0.0928 (5)	H(C4)	0.26	0.127	-0.05
C(5)	0.3941 (5)	0.3610 (8)	0.1069 (6)	H(C5)	0.41	0.415	-0.02
C(6)	0.2802 (5)	0.4916 (7)	0.2302 (6)	H(O1)	0.41	0.22	0.60
O(1)	0.2865 (4)	0.2198 (5)	0.5435 (4)	H(O2)	-0.16	-0.10	0.32
O(2)	-0.0981 (4)	-0.0070 (0)*	0.2387 (4)	H(O5)	0.61	0.24	0.30
O(3)	0.0900 (4)	0.4425 (5)	0.2370 (4)				
O(4)	0.3284 (4)	0.0649 (5)	0.2423 (4)				
O(5)	0.5886 (4)	0.3310 (6)	0.1915 (4)				
O(6)	0.3391 (4)	0.6262 (5)	0.3169 (5)				

* Fixed coordinate kept constant in the least-squares refinement.

Table 3. Anisotropic thermal parameters in β -D-glucurono- γ -lactone

The temperature factor expression used was $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The estimated standard deviations are all less than 0.001.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	0.012	0.010	0.010	-0.001	0.003	0.001
C(2)	0.011	0.008	0.011	-0.002	0.002	-0.001
C(3)	0.010	0.007	0.011	-0.001	0.000	0.001
C(4)	0.011	0.009	0.011	0.001	0.002	0.000
C(5)	0.008	0.013	0.013	0.000	0.001	0.002
C(6)	0.010	0.009	0.015	-0.002	0.000	0.002
O(1)	0.012	0.011	0.013	0.002	-0.002	-0.003
O(2)	0.020	0.011	0.013	-0.008	0.000	0.001
O(3)	0.009	0.006	0.016	0.000	0.001	0.009
O(4)	0.013	0.009	0.013	0.003	0.004	0.001
O(5)	0.007	0.016	0.021	0.000	-0.002	0.001
O(6)	0.013	0.009	0.028	-0.002	0.000	-0.002

Refinement of the structure

The refinement of the positional and thermal parameters was carried out by the full matrix least-squares program of Busing, Martin & Levy (1962). The Hughes (1941) weighting scheme was used for both sets of data and gave final R values of 10.6% and 4.0% for the film and diffractometer data respectively. The final parameters from the diffractometer data are shown in Tables 2, 3 and 4. The corresponding structure factors are given in Table 5, including four low order strong reflections which were omitted from the refinement but were corrected for secondary extinction by Zachariasen's formula (1963). Various weighting schemes were explored for the diffractometer data, and the results are listed in Table 6. Those based on the counting sta-

tistics alone gave e.s.d. that appeared to be somewhat greater than those indicated by the internal consistencies of the molecular parameters determined from the diffractometer data.

A comparison between the final positional parameters obtained from the photographic and diffractometer data is also given in Table 6. Δ_{pa} is the distance between the atomic positions from the two sets of data when the y coordinates were normalized by a shift of 0.0028 so that $\sum_i y_{i,a} = \sum_i y_{i,p}$. The values of $\Delta_{pa}/\sigma(\Delta)$

lie between 1.1 and 3.8, where $\sigma(\Delta) = (\sigma_p^2 + \sigma_a^2)^{\frac{1}{2}}$, suggesting that there are some systematic errors in one set of the results which are not taken into account in the estimated standard deviations. While the value of $Z_{i,p} - Z_{i,a}$ is negligible (0.0007 Å), that of $X_{i,p} - X_{i,a}$

Table 4. Principal axes of thermal ellipsoids

The root mean square displacement U_i corresponds to the i th principal axis of the ellipsoid and $\theta_{ia}, \theta_{ib}, \theta_{ic}$ are angles between the i th axis and the crystallographic axes a, b, c .

The values of U_i in parentheses are from the photographic data.

	i	B^*	U_i	θ_{ia}	θ_{ib}	θ_{ic}
C(1)	1	1.37	0.1320 (134) Å	120.2°	107.0°	32.7°
	2	2.30	0.1711 (168)	94.1	157.4	111.8
	3	2.41	0.1753 (189)	30.5	104.4	66.9
C(2)	1	1.47	0.1367 (124)	45.8	45.0	98.9
	2	1.77	0.1498 (132)	79.4	109.3	159.2
	3	2.47	0.1769 (201)	133.8	51.3	108.6
C(3)	1	1.40	0.1335 (126)	68.7	32.8	114.9
	2	1.86	0.1536 (160)	146.4	84.3	119.7
	3	2.18	0.1663 (170)	114.7	57.9	40.6
C(4)	1	1.68	0.1458 (148)	40.6	108.2	127.9
	2	2.04	0.1606 (157)	82.9	142.4	53.9
	3	2.22	0.1682 (188)	50.3	58.4	58.3
C(5)	1	1.52	0.1386 (129)	3.8	92.4	96.3
	2	2.12	0.1641 (161)	91.7	65.2	154.7
	3	3.09	0.1978 (211)	86.6	24.9	65.6
C(6)	1	1.45	0.1356 (118)	44.2	48.5	105.0
	2	1.94	0.1569 (170)	131.1	57.5	119.4
	3	2.88	0.1907 (213)	103.5	58.5	33.7
O(1)	1	1.77	0.1504 (149)	41.5	89.1	51.8
	2	1.87	0.1536 (158)	63.9	139.4	120.2
	3	3.19	0.2013 (218)	60.3	49.4	127.0
O(2)	1	1.36	0.1315 (134)	55.5	34.5	91.2
	2	2.20	0.1673 (168)	93.6	86.7	172.4
	3	4.81	0.2472 (248)	34.7	124.3	97.5
O(3)	1	1.40	0.1332 (129)	92.9	7.8	97.1
	2	1.70	0.1471 (163)	175.4	92.4	82.8
	3	2.73	0.1861 (179)	86.5	82.5	10.1
O(4)	1	1.50	0.1380 (133)	132.2	45.4	74.1
	2	1.89	0.1546 (162)	75.9	59.4	146.9
	3	3.25	0.2030 (208)	45.6	60.2	61.8
O(5)	1	1.26	0.1267 (113)	12.4	90.7	80.9
	2	3.51	0.2114 (213)	95.9	154.7	65.2
	3	3.83	0.2205 (232)	100.9	64.7	26.6
O(6)	1	1.73	0.1477 (132)	58.6	33.3	81.7
	2	2.64	0.1831 (187)	147.9	57.9	87.7
	3	4.93	0.2501 (244)	95.7	98.2	8.6

* $B = 8\pi^2 U_i^2$.

Table 5 (cont.)

-2	42	44	17	40	-4	21	18	13-	13-	-4	56	55	34-	43	-1	60	58	0	58-	-5	47	52	52	0
-1	19	19	19-	0	-5	24	25	14	21-	-5	90	91	91-	1	-2	79	80	69	40	-1	40	42	42-	0
-2	98	99	99	0	-6	28	27	26-	7	-6	14*	7	7-	2-	-3	19	20	20	0	-2	88	92	75	54-
-3	75	79	79	0	-1	75	79	49-	62-	-1	42	40	0	40	-4	58	55	55	2-	-3	56	61	9	61-
-4	141	138	138-	0	-2	65	61	51-	33-	-2	90	94	94-	9	-5	40	34	19-	28	-4	37	36	11	34-
-5	74	78	78	0	-3	37	40	20	34	-3	86	86	65	57	-6	14*	17	5-	17-	-1	60	62	41-	46
-6	164	176	176	0	-4	65	69	69-	0	-4	91	94	94	9-	-1	107	102	101	11-	-2	38	40	24-	32
-7	60	62	62-	0	-5	91	96	93-	22	-5	31	27	23-	13-	-2	90	92	81-	44-	-3	44	41	4-	41
-1	150	150	130-	74	-1	83	89	82	35	-6	15*	14	10-	9	-3	61	62	12-	61-	-4	44	40	23	33-
-2	141	138	12	137-	-2	31	34	9	33	-1	102	102	4-	102-	-4	95	99	96	25-	-1	81	84	79-	27-
-3	91	89	62	64-	-3	95	95	91	28-	-2	56	54	18	51-	-5	12*	10	4-	9	-2	28	24	17-	17-
-4	143	141	130-	54	-4	56	58	54	21-	-3	116	117	36-	111	-1	91	90	56	71	-3	26	26	26-	2-
-5	51	52	48-	20-	-1	61	68	22	64-	-4	31	30	28-	11-	-2	56	52	45	24-	-4	47	47	24-	41-
-6	53	49	19	44-	-2	35	33	15-	29-	-5	21	19	9-	17-	-3	102	102	74-	70	-1	22	22	22	5
-7	12*	8	5	6	-3	79	81	25	77	-1	120	124	124	4	-4	38	34	33	5-	-2	56	56	50-	25
-1	97	94	74-	58-	-1	116	126	126	0	-2	91	85	1-	85-	-5	61	62	59	17-	-3	42	43	36-	23-
-2	247	251	82	237	-2	31	34	9	33	-3	42	42	31	28	-1	22	23	12-	20	-1	12*	14	11-	9-
-3	42	41	29	29	-2	176	176	176-	0	-4	77	85	67	52	-2	102	93	23-	90-	-3	35	33	9	32-
-4	61	63	34-	52-	-3	54	52	52	0	-5	12*	9	3	8-	-3	35	33	9	32-	-3	17*	17	17	0
-5	100	100	6-	100	-4	47	46	46-	0	-1	72	71	70	11	-4	49	49	31-	37	-1	75	74	74-	0
-6	17*	13	12-	4	-5	130	138	138-	0	-1	72	71	70	11	-1	118	115	33	110	-2	54	58	58	0
-7	12*	9	8	4-	-6	26	23	23-	0	-2	19	14	14	0	-2	61	61	7-	61	-1	30	30	28-	10-
-1	116	118	48	108-	-1	75	74	26-	69	-3	12*	5	5	0	-3	67	67	20	63-	-2	61	59	59-	5
-2	97	91	76	50	-2	199	203	35	200	-1	28	31	3-	31	-1	19	26	26-	2-	-3	22	23	23	4
-3	28	28	27	8	-3	65	66	47-	45	-2	38	35	34	6	-2	8*	9	9-	2-	-1	19	21	18-	10-
-4	24	21	17-	13	-4	68	70	39-	58	-1	31	30	30	0	-1	8*	18	18	0	-2	24	25	16-	19-
-5	22	21	18-	10	-5	54	56	17-	53	-2	28	24	24-	0	-2	106	105	105	0	-1	45	47	7-	47-
-6	22	21	6	20	-6	67	65	46-	45-	-3	91	88	88-	0	-3	42	41	41-	0	-4	51	50	50	0
-1	118	122	108-	55	-1	70	72	34-	64-	-4	42	39	39-	0	-4	51	50	50	0	-1	45	47	7-	47-
-2	77	76	75	11	-2	75	79	79	7-	-5	33	33	33-	0	-4	51	50	50	0	-1	45	47	7-	47-
-3	53	49	30-	38	-3	98	101	100	9	-6	37	36	36-	0	-4	51	50	50	0	-1	45	47	7-	47-

Index	F_0	F_c	F_{ex}^{***}
1 0 1	319	406	399
0 1 1	294	368	381
0 0 2	349	449	444
-1 0 1	252	301	306

* unobserved

** suffering from secondary extinction

*** corrected for secondary extinction

is 0.008 Å. An allowance for this systematic 'discrepancy' between the two sets of parameters would reduce all the Δ_{pd} values below the 3σ (possibly significant) level. Similar results were observed from the comparison of the thermal parameters. Of the 72 B_{ij} values, the ratio of the differences between the photographic and diffractometer results, $\Delta\beta_{pd}$, to the standard deviations, $\sigma(\beta)$, was less than 3.0, except for two values; for $O(2)\beta_{22}$, 3.09 and $O(3)\beta_{22}$, 4.73. However, the comparison of the corresponding U_i values in Table 4, where the photographic results are shown in parentheses, would not reveal the fact that the discrepancies for these atoms are outstanding.

Although the hydrogen atoms were not located on the difference synthesis using the photographic data, they were clearly revealed with the diffractometer data at reasonable locations with respect to the carbon and oxygen atoms. Their positional parameters were not refined and they were assigned the same thermal parameters as those of the carbon or oxygen atoms to which they were bonded.

Description of the structure

The shape of the molecule and identification of the atoms are shown in Fig. 2. The numbering is based on the convention used for glucuronic acid from which the compound is derived. The molecule consists of

fused lactone and furanose rings making a dihedral angle of 111.3° between plane I and plane II as defined in Fig. 2. The furanose ring has the characteristic non-planar envelope configuration, in which one atom, C(1), is out of the plane of the other four by 0.52 Å. This displacement is in the *endo* direction, *i.e.* towards the dihedral angle. The angle between the plane C(2)C(1)-O(4) and that of the four atoms C(2)C(3)C(4)O(4) is 144.6° . In the lactone ring, four atoms, C(4)C(3)O(3)-C(6) are planar within an observed 0.003 Å. The fifth atom, C(5), is displaced by 0.25 Å from this plane, I, in the *exo* direction with respect to the dihedral angle between the rings. The carbonyl group of atoms, C(5)-O(3)C(6)O(6), is also planar within 0.003 Å. This plane has a dihedral angle of 10.7° with plane I. The bond lengths and valence angles in the molecule are given in Table 7. The C-C bond lengths range from 1.511 to 1.533 Å, and none differ from the mean value of 1.522 Å by more than 3σ . This is in excellent agreement with the mean value of 1.523 Å for 18 C-C bonds in the furanose derivatives reported by Sundaralingam (1965). There is no evidence that the C(5)-C(6) bond, which has sp^3-sp^2 orbital character by reason of the carbonyl group, is significantly shorter than an sp^3-sp^3 bond, such as C(1)-C(2), for example, as suggested by Dewar & Schmeising (1959) in their discussion of the effects of orbital hybridization on bond lengths. The C-OH bonds are 1.409, 1.413, 1.416 Å and again there

Table 6. Comparison of photographic and diffractometer data

Weighting scheme used	Photographic		Diffractometer		Counting statistics*
	Hughes	Hughes	Cruikshank	Hughes	
Final <i>R</i> index	0.106	0.040	0.041	0.055	0.055
Weighted <i>R</i> index	0.152	0.053	0.055	0.050	0.050
Greatest e.s.d. in atomic coordinates (Å)	0.006	0.004	0.005	0.009	0.009
	$\Delta p\sigma$	$\sigma_{\Delta}^{\dagger}$	$\Delta p\sigma/\sigma_{\Delta}$		
C(1)	0.0130 Å	0.0067 Å	1.9		
C(2)	0.0231	0.0066	3.5		
C(3)	0.0215	0.0066	3.2		
C(4)	0.0124	0.0074	1.7		
C(5)	0.0148	0.0073	2.0		
C(6)	0.0150	0.0076	2.0		
O(1)	0.0072	0.0059	1.2		
O(2)	0.0222	0.0059 [‡]	3.7		
O(3)	0.0180	0.0055	3.3		
O(4)	0.0067	0.0059	1.1		
O(5)	0.0146	0.0060	2.4		
O(6)	0.0184	0.0066	2.8		

* $\frac{1}{w} = \left(k \cdot \frac{1}{Lp}\right)^2 (s + tB)$ where k = scale factor, s = scan count, B = background count, t = time ratio of scan to background.

[†] $\sigma_{\Delta}^2 = \sigma_p^2 + \sigma_a^2$ (both using Hughes weighting).

[‡] Fixed y parameter, $\sigma = \bar{\sigma}_{oxy}$.

Table 7. Bond angles and lengths

The estimated standard deviations given in parentheses refer to the last decimal positions of respective values.

<i>i</i>	<i>j</i>	<i>D</i> (<i>ij</i>)	<i>i</i>	<i>j</i>	<i>k</i>	Angle <i>ijk</i>
C(1)	C(2)	1.520 (6) Å	O(1)	C(1)	C(2)	108.0 (3)°
C(2)	C(3)	1.520 (6)	O(1)	C(1)	O(4)	110.8 (3)
C(3)	C(4)	1.533 (6)	C(2)	C(1)	O(4)	104.8 (3)
C(4)	C(5)	1.526 (6)	C(1)	C(2)	C(3)	102.0 (3)
C(5)	C(6)	1.511 (6)	C(1)	C(2)	O(2)	112.0 (3)
C(1)	O(1)	1.413 (5)	C(3)	C(2)	O(2)	106.4 (3)
C(2)	O(2)	1.409 (5)	C(2)	C(3)	O(3)	108.7 (3)
C(5)	O(5)	1.416 (5)	C(2)	C(3)	C(4)	104.8 (3)
C(1)	O(4)	1.424 (5)	C(4)	C(3)	O(3)	106.2 (3)
C(4)	O(4)	1.446 (5)	C(3)	C(4)	O(4)	106.1 (3)
C(3)	O(3)	1.475 (5)	C(3)	C(4)	C(5)	104.9 (3)
C(6)	O(3)	1.340 (5)	C(5)	C(4)	O(4)	110.4 (3)
C(6)	O(6)	1.215 (5)	C(4)	C(5)	C(6)	104.0 (3)
			C(4)	C(5)	O(5)	115.0 (3)
			C(6)	C(5)	O(5)	112.3 (3)
			C(5)	C(6)	O(3)	111.0 (3)
			C(5)	C(6)	O(6)	128.9 (4)
			O(3)	C(6)	O(6)	120.0 (4)
			C(3)	O(3)	C(6)	111.0 (3)
			C(1)	O(4)	C(4)	108.7 (3)

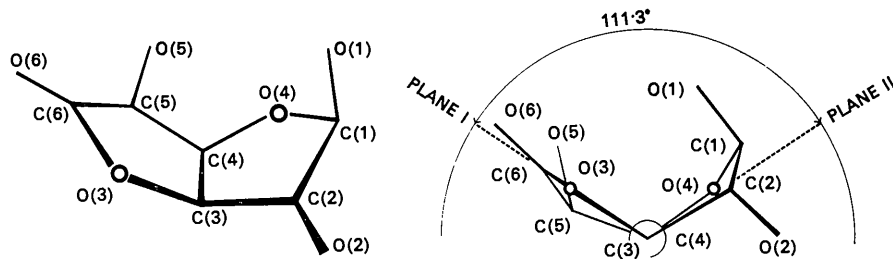


Fig. 2. Numbering of the atoms in the molecule (left) and geometry of the molecule viewed along the direction of the C(3)–C(4) bond (right).

is no significant difference from the mean value of 1.413 Å. The C=O bond is 1.215 Å, which is within the range of expected values for the carbonyl group. The ring C-O distances range from 1.340 to 1.475 Å. In the furanose ring they are normal and equal within 2σ to a mean value of 1.435 Å, but in the lactone ring the difference is 0.135 Å, which is $19\frac{1}{2}\sigma_{C-O}$. This shows that there is a small but significant contribution from the valence-bond resonance form (V). Thus, the lactone ring is different from the furanose ring by reason of its bond character, in addition to its closer approach to planarity.

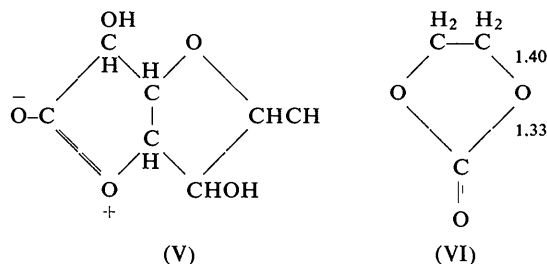
The valence bond resonance character of the R-C-O-R group leading to a difference of about 0.1 Å



in the bond lengths on either side of the ether oxygen has also been observed in ethylene carbonate (VI) (Brown, 1954), and in the alkaloid derivatives, himbacine hydrobromide (Fridrichsons & Mathieson, 1962) and jacobine bromodilactone (Mathieson & Taylor, 1961). However this does not necessarily im-

pose strict planarity on the whole lactone group, since

C(3) is 0.25 Å out of the plane of the C-C-O group.



The ring angles at the carbon atoms range from 102.0 to 106.3° with the exception of that at the carbonyl atom, C(6), which is larger, 110.0°, as would be expected from the sp^2 hybridization of the carbon atom. The ring oxygen atoms have internal angles of 108.7 and 111.0°. The external C-C-OH angles to the rings range from 106.4 to 114.3°.

Table 8. Comparison of molecular geometry in galactono- γ -lactone (1) and glucurono- γ -lactone (2)

	(1)	(2)
C-C	1.502-1.546 Å Mean 1.525	1.511-1.533 Å Mean 1.522
Acyclic >C(H)-O(H)	1.405-1.418 Mean 1.411	1.409-1.416 Mean 1.413
Acyclic-C(H ₂)-O(H)	1.447	—
C=O	1.198	1.215
Lactone ring C-O	1.358	1.340
Furanose ring C-O	1.464	1.475
Lactone group	Planar within 0.03 Å	Non-planar displacement 0.25 Å
Lactone ring	Non-planar with displacement of 0.64 Å	Non-planar with displacement of 0.25 Å
Furanose ring	—	Non-planar with displacement of 0.50 Å
Ring angles at O, >C=O, C (mean)		
Lactone ring	109°, 110°, 102°	111°, 111°, 105°

Comparison of conformation angles in lactone and furanose rings

The atomic numbering is that given in the original papers. C(1)→C(2) in galactonolactone, for example, refers to the dihedral angle about the bond C(1)-C(2) formed by the adjacent bonds in the ring, *i.e.* O(4)-C(1) and C(2)-C(3), when C(1) is above C(2) and the + direction is anticlockwise.

Lactone rings		Galactonolactone (Jeffrey, Rosenstein & Vlasse, 1967)	
Glucuronolactone (this paper)		Glucuronolactone (this paper)	
C(5) → C(6)	-15.8°	C(3) → C(4)	-38.5°
C(6) → O(3)	10.4	C(4) → O(4)	27.7
O(3) → C(3)	-0.5	O(4) → C(1)	-4.8
C(3) → C(4)	-9.3	C(1) → C(2)	-20.4
C(4) → C(5)	14.5	C(2) → C(3)	35.1
Furanose rings		Sucrose (Brown & Levy, 1963)	
Glucuronolactone (this paper)		Sucrose (Brown & Levy, 1963)	
C(1) → C(2)	-35.8°	C(3) → C(4)	-35.0°
C(2) → C(3)	26.2	C(4) → C(5)	27.3
C(3) → C(4)	-8.7	C(5) → O(2)	-8.2
C(4) → O(4)	-14.7	O(2) → C(2)	-14.6
O(4) → C(1)	32.1	C(2) → C(3)	31.1

Table 9. *Intermolecular distances in β -D-glucurono- γ -lactone*

Hydrogen-bond distances and angles (with their estimated standard deviations in parentheses)

<i>i</i>	<i>j</i>	<i>k</i>	<i>D</i> (<i>ij</i>)	<i>D</i> (<i>jk</i>)	Angle <i>ijk</i>
C(6)	O(6)	O(1, <i>a</i>)		2.730 (5) Å	130.2 (3)°
O(6)	O(1, <i>a</i>)	C(1, <i>a</i>)	2.730 (5) Å		107.4 (3)
O(6)	O(1, <i>a</i>)	O(2, <i>b</i>)	2.730 (5)	2.839 (4)	116.7 (2)
C(1, <i>a</i>)	O(1, <i>a</i>)	O(2, <i>b</i>)		2.839 (4)	132.9 (3)
O(1, <i>a</i>)	O(2, <i>b</i>)	C(2, <i>b</i>)	2.839 (4)		124.7 (3)

Non-bonded distances less than 3.3 Å between carbon and oxygen atoms

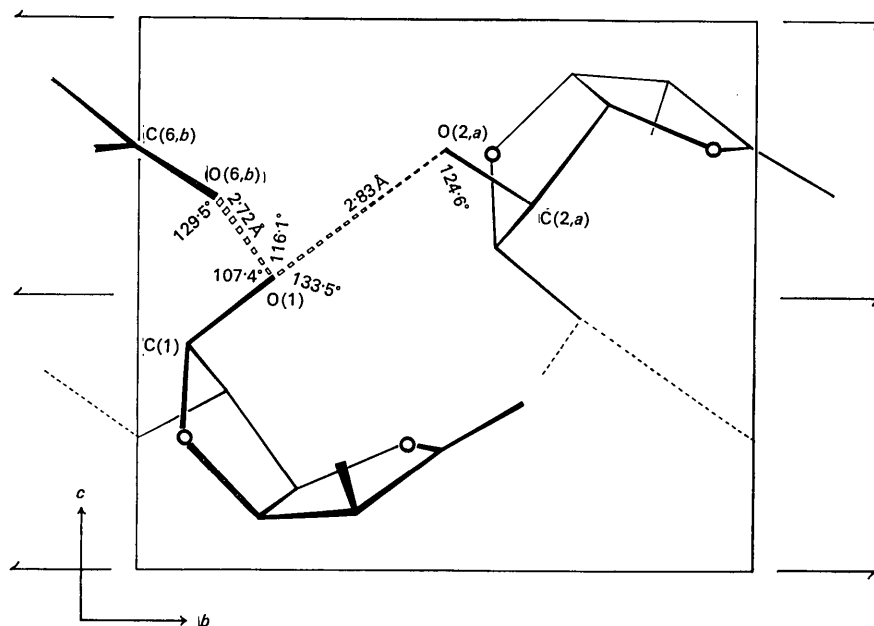
<i>i</i>	<i>j</i>	<i>D</i> (<i>ij</i>)
C(2)	O(5, <i>c</i>)	3.256 Å
C(3)	O(2, <i>d</i>)	3.157
C(3)	O(5, <i>c</i>)	3.241
C(4)	O(2, <i>d</i>)	3.264
C(5)	O(2, <i>d</i>)	3.098
C(6)	O(2, <i>d</i>)	3.255
O(3)	O(2, <i>d</i>)	3.168

Closest non-bonding distances to H(O5), of the hydroxyl group not involved in hydrogen bonding

<i>i</i>	<i>j</i>	<i>D</i> (<i>ij</i>)
H(O5)	H(C2, <i>e</i>)	2.25 Å
	H(C1, <i>f</i>)	2.52
	O(6, <i>f</i>)	2.67
	O(2, <i>e</i>)	2.75
	C(2, <i>e</i>)	2.78
	H(O2, <i>e</i>)	2.98

Symmetry code

	<i>x</i>	<i>y</i>	<i>z</i>
-	<i>x</i>	<i>y</i>	<i>z</i>
<i>a</i>	1 - <i>x</i>	$\frac{1}{2} + y$	1 - <i>z</i>
<i>b</i>	1 + <i>x</i>	1 + <i>y</i>	<i>z</i>
<i>c</i>	-1 + <i>x</i>	<i>y</i>	<i>z</i>
<i>d</i>	- <i>x</i>	$\frac{1}{2} + y$	- <i>z</i>
<i>e</i>	1 + <i>x</i>	<i>y</i>	<i>z</i>
<i>f</i>	1 - <i>x</i>	$-\frac{1}{2} + y$	1 - <i>z</i>

Fig. 3. The crystal structure viewed along the *a* axis. Broken lines represent hydrogen bonds.

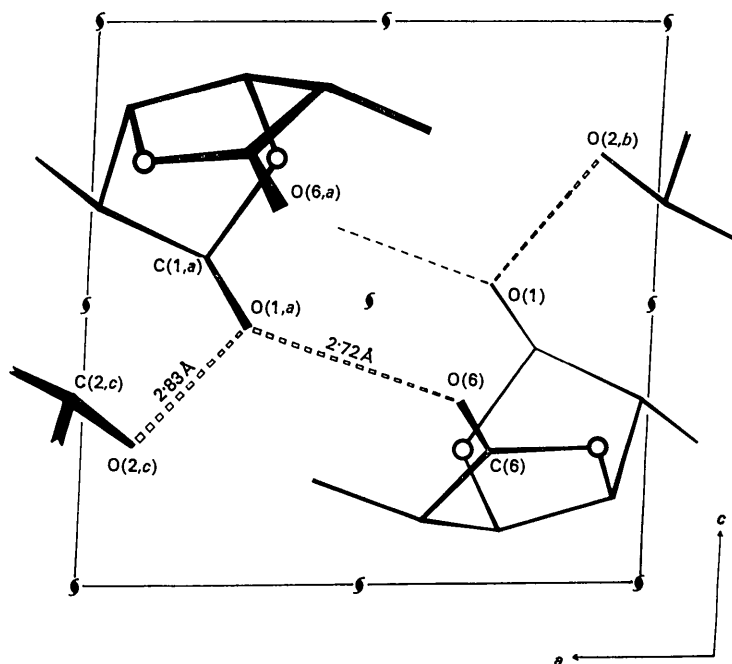


Fig. 4. The crystal structure viewed along the b axis. Broken lines represent hydrogen bonds.

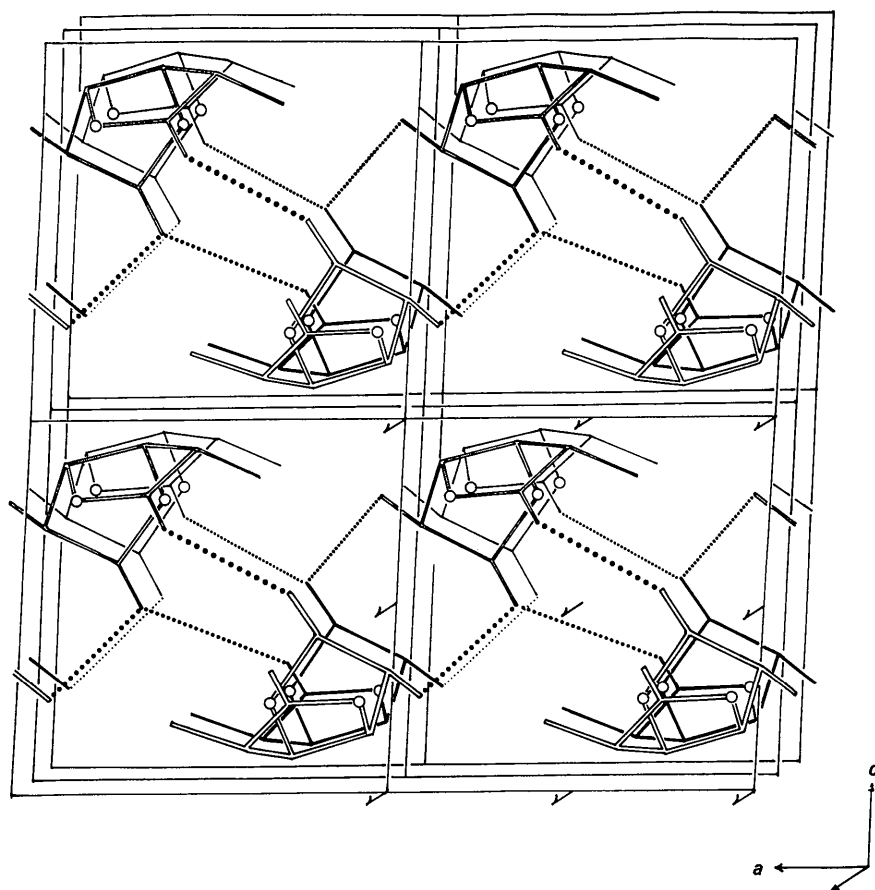


Fig. 5. Perspective drawing of the crystal structure showing the double layer character.

The comparison with the molecular geometry of the galactono- γ -lactone (Jeffrey, Rosenstein & Vlasse, 1967), which is a monocyclic lactone, is shown in Table 8. With the exception of the detailed shape of the lactone rings, the correspondence is very close. The difference in the shape of the rings is shown more clearly by comparing the conformation angles, which are also given in Table 8. From these data, it is interesting to note that the furanose ring in glucuronolactone has the same conformation angles within about 1° as those in sucrose, despite its fusion to a lactone ring. The angles in the lactone ring in galactonolactone are also similar, with somewhat larger differences of the order of 5° . In contrast, the fused lactone ring in glucuronolactone has quite different conformation angles, which must be associated with the same strain energy factors which result in the non-planarity of the lactone group.

The molecules are associated in the crystal by the very simple system of hydrogen-bonding shown in Figs. 3, 4 and 5. The O(H)···O distances and the corresponding angles are given in Table 9. The O(1)H is a hydrogen-bond donor to the carbonyl oxygen, O(6), at 2.730 Å, and hydrogen-bond acceptor from O(2)H at 2.839 Å. This almost planar group of atoms, C(1)–O(1), O(2) and O(6) then links the molecules into double layers parallel to (001). The van der Waals distances between these double layers correspond with the marked (001) cleavage. Of the three hydroxyl groups which might be expected to form hydrogen bonds, O(1)H participates in two, one as donor and one as acceptor, O(2)H in one as donor, and O(5)H in none. The hydrogen atoms lie at 0.05 and 0.24 Å off the line of centers of the two O(H)···O bonds. The O(5)H hydroxyl is not engaged in hydrogen-bonding and the closest intermolecular contacts to H(O5) are shown in Table 9.

The non-bonding intermolecular distances involving oxygen and carbon atoms are given in Table 9. None are especially short. In the α -form, in which the adjacent hydroxyl groups O(1) and O(2) are both *exo* to the ring, the non-bonding O···O separation would be about 2.6 Å, *i.e.* significantly shorter than the corresponding distance in the observed β form, where the O(1)···O(2) separation is 3.6 Å. This, rather than the crystal lattice forces, may be the stereochemical factor favoring the mutarotation to the β anomer, in the preparation from the α -isopropylidene derivative.

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pylidene-D-glucufuranuronate. The automatic diffractometer used in this research was provided by an equipment grant from the National Science Foundation.

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