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THE CRYSTAL STRUCTURE OF D-GLUCONIC ACID MONOHYDRATE

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ABSTRACT

D-Gluconic acid monohydrate, obtained in crystalline form by slow evaporation of an aqueous solution, is monoclinic, space group $P2_1$, with $a = 8.430(9)$, $b = 5.403(6)$, $c = 10.406(9)$ Å, $\beta = 96.88(6)°$, and $Z = 2$. The crystal structure was determined from three-dimensional X-ray diffraction data taken on an automatic diffractometer with MoKα, and refined by least-squares techniques to $R = 0.045$ for 1018 reflexions. The molecules of D-gluconic acid exist in a bent-chain conformation similar to that found in ammonium D-gluconate. All of the oxygen atoms participate in intermolecular hydrogen bonds utilising all oxygen-bonded hydrogen atoms, and the water molecule connects four different acid molecules.

INTRODUCTION

D-Gluconic acid equilibrates in aqueous solutions to give a mixture of the acid and the γ- and δ-lactones[1,2]. The δ-lactone is the form most commonly available commercially, and its crystal structure has been determined[3]. D-Gluconic acid is difficult to crystallise, but has been reported[4] to form long needles, with m.p. 125°, which decomposed at 132–133°. Usually, D-gluconic acid is commercially available as a 50% aqueous solution or in the form of syrup. The γ-lactone has long been known[1] in crystalline form.

Because of the interest in the molecular conformation of acyclic D-gluconic acid, several investigations of its crystalline salts have been carried out using X-ray and neutron diffraction techniques. In the crystals of potassium[5], potassium monohydrate (two forms)[6], manganese(II) dihydrate[7], ammonium[8], sodium[9], and lead(II)[9] D-gluconate, various zigzag and bent-chain conformations were found. The results of a study of the crystal structure of D-gluconic acid monohydrate are now reported.

EXPERIMENTAL

Crystals of D-gluconic acid monohydrate were obtained by very slow (2–3 months) concentration of an aqueous solution of commercial D-glucono-δ-lactone.

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The crystals were clear plates, m.p. 125–126° with decomposition at ~240°, with *c* perpendicular to, and *a* and *b* along, the broad face. They decomposed a little in air.

Anal. Calc. for $C_6H_{12}O_7 \cdot H_2O$: C, 33.6; H, 6.6. Found: C, 33.9; H, 6.5.

Weissenberg and oscillation photographs showed the crystals to be monoclinic, and space group $P2_1$ was indicated by the systematic absence of reflexions $0k0$ with k odd. A crystal fragment, having the approximate dimensions 0.25 × 0.55 × 0.04 mm, was cut from a large crystal and sealed in a capillary. A Syntex $P2_1$ diffractometer, MoKα radiation (λ 0.71069 Å), and a graphite monochromator were used for lattice-parameter and intensity measurements at T = 301 ±2 K. Measurements were made for 1858 symmetry-independent reflexions having $2\theta \leqslant 65°$ by the 2θ–ω scan technique. Two reflexions, which were monitored periodically, exhibited no significant variations in intensity during the period of data collection. The intensities were corrected for Lorentz and polarisation factors, and empirical absorption corrections were made from φ-scan data. The crystal data are listed in Table I.

The structure was solved by direct methods using the MULTAN programs of the "X-Ray" system (1978 version)[10]; 250 reflexions with $E \geqslant 1.13$ were used to generate and refine 16 different sets of re-normalised structure-factor phases. For those phase sets having the "best" associated figures of merit, E-maps were computed. None of the maps, however, revealed a plausible molecular structure. Therefore, a non-routine procedure was employed. The 21 highest peaks from the best map were used as the starting model. During the refinement, using full-matrix least-squares techniques, the "atoms" having high values of B_{iso}, as well as those with unrealistic interatomic distances, were removed from further calculations. In this way, the number of "atoms" was reduced to 12 and R dropped to 0.32. Two remaining heavy atoms were found from a difference synthesis. Further refinement, first with isotropic, and then anisotropic, thermal parameters, gave R 0.074. A difference synthesis at this stage showed all H atoms. They were included with isotropic temperature factors, and three cycles of full-matrix refinement yielded a

TABLE I

CRYSTAL DATA FOR D-GLUCONIC ACID MONOHYDRATE

Stoichiometry	$C_6H_{12}O_7 \cdot H_2O$
Z	2
Space group	$P2_1$
a	8.430(9) Å
b	5.403(6) Å
c	10.406(9) Å
β	96.88(6)°
ρ (calculated)	1.51 g cm^{-3}
ρ (observed)[a]	1.52 g.cm^{-3}
μ (MoKα)	1.5 cm^{-1}

[a]The density was measured by flotation in a mixture of chloroform and carbon tetrachloride

final R value of 0.045 and an R_w value of 0.035 for 1018 reflexions with $I > 2\sigma(I)$, where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with $w = \sigma^{-2}(F_o)$, where $\sigma(F_o)$ was from counting statistics. During the last cycle of refinement, no parameter shifted more than one-fourth of its standard deviation. A final difference synthesis was featureless.

All calculations, except MULTAN, were performed on a NOVA 1200 computer with the Syntex XTL/XTLE Structure Determination System (1976)[11]. Neutral-atom scattering factors were those listed in International Tables for X-ray Crystallography (1974)[12]. The anomalous dispersion was included for O atoms.

TABLE II

THE FINAL ATOM CO-ORDINATES AND ISOTROPIC THERMAL PARAMETERS, WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES[a]

Atom	x	y	z	B_{eq} *or* B_{iso}
O-1	0.3079(4)	0.6825(10)	0.0979(3)	3.52(26)
O-1′	0.1717(4)	0.3386(9)	0.0423(3)	3.15(25)
O-2	0.4945(4)	0.6(fixed)	−0.0965(3)	2.76(24)
O-3	0.3098(4)	0.6371(9)	−0.3274(3)	3.28(26)
O-4	0.1008(4)	0.2723(8)	−0.3161(3)	2.33(21)
O-5	−0.0746(4)	0.8806(9)	−0.2700(3)	2.44(22)
O-6	−0.2862(4)	0.6995(10)	−0.4829(3)	2.77(24)
O-7	0.5393(4)	1.0106(10)	−0.3485(4)	3.31(26)
C-1	0.2737(5)	0.5137(11)	0.0218(4)	2.16(28)
C-2	0.3401(5)	0.4897(12)	−0.1067(4)	2.05(28)
C-3	0.2340(5)	0.6263(11)	−0.2135(4)	1.91(28)
C-4	0.0751(5)	0.5016(11)	−0.2531(4)	1.78(26)
C-5	−0.0386(5)	0.6665(10)	−0.3410(4)	1.81(27)
C-6	−0.1962(5)	0.5457(11)	−0.3897(4)	2.25(32)
H-11	0.138(7)	0.383(13)	0.140(6)	8.1(16)
H-22	0.555(7)	0.461(16)	−0.079(6)	9.3(21)
H-33	0.378(5)	0.723(9)	−0.316(4)	1.1(10)
H-44	0.157(6)	0.297(10)	−0.383(5)	4.9(13)
H-55	−0.020(5)	0.983(10)	−0.282(4)	2.0(11)
H-66	−0.325(6)	0.828(11)	−0.455(5)	5.6(17)
H-7	0.467(6)	1.097(11)	−0.402(5)	5.3(14)
H-7′	0.581(6)	1.095(12)	−0.281(5)	5.3(15)
H-2	0.344(5)	0.325(10)	−0.132(4)	2.0(9)
H-3	0.222(4)	0.780(8)	−0.180(3)	0.4(7)
H-4	0.023(4)	0.473(8)	−0.180(3)	0.7(7)
H-5	0.011(5)	0.717(8)	−0.421(3)	1.9(8)
H-6	−0.183(5)	0.413(9)	−0.436(4)	1.7(9)
H-6′	−0.251(4)	0.509(9)	−0.313(4)	2.1(8)

[a]For non-H atoms, $B_{eq} = \frac{1}{3}(B_{11} + B_{22} + B_{33})$. The *y* co-ordinate of O-2 was not refined.

TABLE III

BOND LENGTHS (Å), BOND ANGLES (DEGREES), AND TORSION ANGLES (DEGREES) IN D-GLUCONIC ACID MONOHYDRATE

Bond	*Bond distance*	*Bond*	*Bond distance*
C-1–O-1	1.220(7)	C-1–O-1′	1.313(6)
C-2–O-2	1.424(5)	C-3–O-3	1.414(5)
C-4–O-4	1.430(7)	C-5–O-5	1.425(6)
C-6–O-6	1.425(6)	C-1–C-2	1.516(5)
C-2–C-3	1.530(6)	C-3–C-4	1.512(6)
C-4–C-5	1.529(6)	C-5–C-6	1.512(6)

Bonds	*Bond angle*	*Bonds*	*Bond angle*
O-1–C-1–O-1′	122.8(5)	O-1–C-1–C-2	123.6(5)
C-2–C-1–O-1′	113.6(4)	C-1–C-2–O-2	109.2(4)
C-1–C-2–C-3	110.7(4)	O-2–C-2–C-3	107.6(4)
C-2–C-3–C-4	113.9(4)	C-2–C-3–O-3	110.2(4)
O-3–C-3–C-4	105.3(4)	C-3–C-4–O-4	109.5(4)
C-3–C-4–C-5	112.0(4)	O-4–C-4–C-5	110.5(4)
C-4–C-5–O-5	108.7(4)	C-4–C-5–C-6	114.3(4)
O-5–C-5–C-6	106.9(4)	C-5–C-6–O-6	110.6(4)

Bonds	*Torsion angle*	*Bonds*	*Torsion angle*
C-1–C-2–C-3–C-4	−71.4(6)	C-2–C-3–C-4–C-5	169.5(6)
C-3–C-4–C-5–C-6	176.8(5)	O-2–C-2–C-3–C-4	169.4(5)
C-4–C-5–C-6–O-6	−172.8(6)	O-1–C-1–C-2–O-2	29.2(8)
O-2–C-2–C-1–O-1′	152.6(7)	C-2–C-1–O-1′–H-11	179(4)

RESULTS AND DISCUSSION

The final atomic* parameters are listed in Table II; interatomic distances and angles for the D-gluconic acid molecule are given in Table III.

The gluconic acid molecule is shown in Fig. 1, which also gives the thermal ellipsoids and the atomic notation. The molecule has a bent-chain conformation with no intramolecular hydrogen bonds. This conformation can be derived from the planar conformation of the D-gluconate ion found in potassium D-gluconate monohydrate (monoclinic modification)[13] by rotating ~120° about the C-2–C-3 bond. This rotation gives a conformation in which C-2,3,4,5,6 and O-2,6 lie in a plane (Table III). This results in the D-gluconic acid molecule having the bent-chain conformation similar to that found for ammonium D-gluconate[8]. The only

*The Tables of observed, and calculated, structure factors and of anisotropic, thermal parameters may be obtained from the author, or from Elsevier Scientific Publishing Company, BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/260/*Carbohydr. Res.*, 122 (1983) 23–29

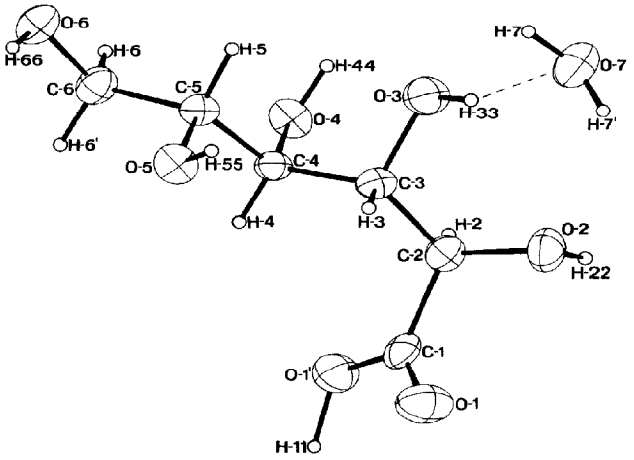

Fig. 1. Atomic notation and thermal ellipsoids[15] (50% probability) for D-gluconic acid monohydrate.

difference involves O-6, which is antiperiplanar in the acid and synclinal in the ammonium salt. The C–COO group is planar. There is also a tendency for H-11 to lie in this plane (Table III). In contrast to most other α-hydroxycarboxylic moieties[14], the -C(OH)COOH group is not planar [the torsion angles O-1–C-1–C-2–O-2 and O-1'–C-1–C-2–O-2 are 29.2(8)° and −152.6(7)°, respectively]. A similar situation has been observed for ammonium D-gluconate. In comparing the conformation of D-gluconic acid and that of its δ-lactone[3], it is easy to transform a model of the gluconic acid by rotation of 120° about the C-3–C-4 bond and to eliminate a molecule of water to produce the δ-lactone.

The C–C bond-lengths (Table III) range from 1.512(6) to 1.530(6), and those for C–O (alcohol) from 1.414(5) to 1.430(7) Å; the differences from the mean are not significant. The same is true for the valence angles; the mean value for the C–C–C angles is 113°, and for C–C–O is 109°. These results are in good agreement with those found for the salts of D-gluconic acid[5–9].

The crystal packing down the b axis is shown in Fig. 2. The D-gluconic acid molecules are oriented in the crystal with their long molecular axis approximately parallel to the $a + c$ vector. The molecular packing in the crystal appears to be determined by hydrogen-bonding effects, since there are eight hydrogen bonds per asymmetric unit. Hydrogen-bonding distances and angles are listed in Table IV. All of the oxygen atoms participate in intermolecular hydrogen bonds utilising all oxygen-bonded hydrogen atoms, and the water molecules are hydrogen-bonded to four symmetry-related gluconic acid molecules. As shown in Table IV, the shortest

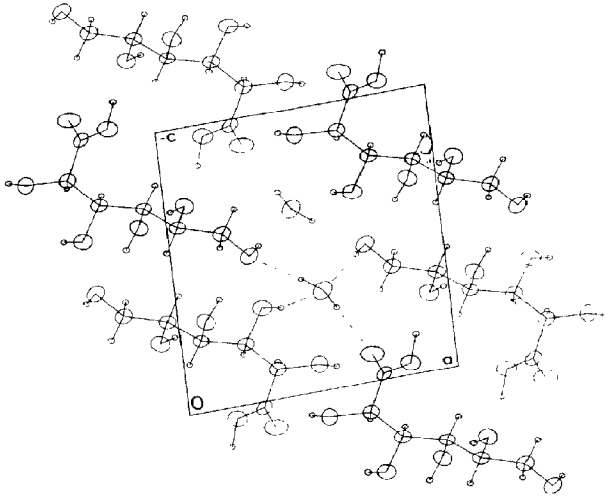

Fig. 2. Molecular packing in the crystal structure of D-gluconic acid monohydrate viewed down the *b* axis.

hydrogen bond [2.607(4) Å] is that from the carboxyl group (as donor group) to the hydroxyl group.

TABLE IV

HYDROGEN-BOND DISTANCES (Å) AND ANGLES (DEGREES)

O–H · · · O	*O · · · O*	*O–H*	*H · · · O*	*O–H · · · O*
O-1′–H-11 · · · O-5[a]	2.607(4)	1.11(6)	1.51(6)	166(6)
O-2–H-22 · · · O-1[b]	2.806(5)	0.91(8)	1.92(8)	162(7)
O-3–H-33 · · · O-7	2.822(6)	0.74(4)	2.12(4)	160(4)
O-4–H-44 · · · O-6[c]	2.785(4)	0.90(5)	1.94(5)	155(5)
O-5–H-55 · · · O-4[d]	2.658(4)	0.74(5)	1.92(5)	173(5)
O-6–H-66 · · · O-7[e]	2.727(6)	0.84(6)	1.95(6)	154(6)
O-7–H-7 · · · O-6[f]	2.788(5)	0.91(6)	1.90(5)	165(5)
O-7–H-7′ · · · O-1[g]	2.919(5)	0.88(6)	2.08(5)	161(5)

[a]Symmetry code, $-x,y-1/2,-z$; [b]$1-x,y-1/2,-z$; [c]$-x,y-1/2,-1-z$; [d]$x,1+y,z$; [e]$x-1,y,z$; [f]$-x,1/2+y,-1-z$; [g]$1-x,1/2+y,-z$.

REFERENCES

1 J. U. NEF, *Justus Liebigs Ann. Chem.*, 403 (1914) 204–337.
2 D. T. SAWYER, *Chem. Rev.*, 64 (1964) 633–643.
3 M. L. HACKERT AND R. A. JACOBSON, *Acta Crystallogr., Sect. B*, 27 (1971) 203–209.
4 K. REHORST, *Ber.*, 63 (1930) 2279–2292.
5 C. D. LITTLETON, *Acta Crystallogr.*, 6 (1953) 775–781.
6 N. C PANAGIOTOPOULOS, G. A. JEFFREY, S. J LA PLACA, AND W. C. HAMILTON, *Acta Crystallogr., Sect. B*, 30 (1974) 1421–1430
7 T LIS, *Acta Crystallogr., Sect. B*, 35 (1979) 1699–1701.
8 T LIS, *Acta Crystallogr., Sect. B*, 37 (1981) 1957–1959.
9 T. LIS, unpublished results.
10 G. GERMAIN, P. MAIN, AND M. M. WOOLFSON, *Acta Crystallogr., Sect. A*, 27 (1971) 368–376.
11 *Syntex XTL/XTLE Structure Determination System*, Syntex Analytical Instruments, Cupertino, 1976.
12 *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, 1974.
13 G. A. JEFFREY AND E. J. FASISKA, *Carbohydr Res.*, 21 (1972) 187–199.
14 M. D. NEWTON AND G A. JEFFREY, *J. Am. Chem Soc.*, 99 (1977) 2413–2421.
15 C. K. JOHNSON, *ORTEP II, Report ORNL-5138*, Oak Ridge National Laboratory, Tennessee, 1976.