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The crystal structure of α-D-glucopyranosyl potassium hydrogenphosphate

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ABSTRACT

The title compound, when crystallised from water, is orthorhombic, space group $P2_12_12_1$, with unit cell dimensions $a = 7.351(4)$, $b = 9.666(6)$, $c = 15.230(7)$ Å, and $Z = 4$. The α-D-glucopyranosyl ring adopts the $^4C_1$ conformation, the P–O-1–C-1–C-2 and P–O-1–C-1–O-5 torsion angles are −174.6(5) and 63.7(4)°, respectively, and the length of the P–O-1 bond [1.596(2) Å] is shorter than such bonds in doubly ionised α-D-glucopyranosyl phosphates. The crystal structure is stabilised by a three-dimensional hydrogen-bonding network that utilises all of the hydroxyl groups. The potassium ion has six-fold co-ordination involving oxygens atoms of five different α-D-glucopyranosyl phosphate monoanions.

INTRODUCTION

α-D-Glucopyranosyl dihydrogenphosphate [α-D-glucose 1-(phosphoric acid), G1P] is an important intermediate in the metabolism of carbohydrates. Depending on the pH, G1P may also exist as a mono- or di-anion. Of these three forms, only the crystal structure of the dianion as the sodium[1] and potassium[2] salt has been reported. The second, orthorhombic form of potassium G1P was also studied[3], but the structural details have not been published. The structure of the monoanion in the crystalline monopotassium salt is now reported in a continuation of studies[4] of the structure of organic phosphate esters in relation to their states of ionisation.

EXPERIMENTAL

α-D-Glucopyranosyl dihydrogenphosphate was prepared from commercially available $K_2G1 \cdot P2H_2O$ (Reanal) by ion exchange on Dowex 50 W (H^+) resin and an equimolar amount of α-D-glucopyranosyl dipotassium phosphate dihydrate was added to the solution. Slow concentration of the resulting solution gave many-faced

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TABLE I

Crystal data for α-D-glucopyranosyl potassium hydrogenphosphate

Stoichiometry $C_6H_{12}O_9P^- \cdot K^+$; $M_r = 298.23$;
$a = 7.351(4)$, $b = 9.666(6)$, $c = 15.230(7)$ Å;
$V = 1082(2)$ Å^3; D(calc.) = 1.830(3) g·cm^{-3}; $Z = 4$;
D(measured)[a] = 1.81 g·cm^{-3};
μ(Mo-K_α) = 6.8 cm^{-1}; $F(000) = 616$.

[a] The density was measured in a mixture of CCl_4 and CH_2Br_2.

colourless prisms suitable for X-ray studies. Weissenberg and oscillation photographs showed the crystals to be orthorhombic, and the space group $P2_12_12_1$ was indicated by systematic absence of reflections. A crystal fragment having the approximate dimensions 0.25 × 0.2 × 0.5 mm was cut from a large crystal. A Syntex

TABLE II

Fractional co-ordinates and U_{eq} values (ESD's in parentheses)[a] for crystals of α-D-glucopyranosyl potassium hydrogenphosphate

Atom	x/a	y/b	z/c	U_{eq} or U_{iso} (Å^2)
K	−0.07950(7)	−0.17949(7)	0.29506(4)	0.0266(5)
P	0.31422(8)	0.17445(8)	0.56438(4)	0.0177(5)
O-1	0.14000(20)	0.07667(19)	0.55702(12)	0.021(1)
O-2	−0.10318(26)	−0.07447(22)	0.46270(13)	0.029(1)
O-3	−0.35457(23)	−0.15132(23)	0.60188(15)	0.035(1)
O-4	−0.23929(28)	−0.06230(24)	0.77220(14)	0.035(1)
O-5	0.19161(22)	−0.10547(20)	0.65519(12)	0.022(1)
O-6	0.16322(30)	−0.22559(23)	0.82377(14)	0.034(1)
O-7	0.46601(22)	0.08419(21)	0.51915(13)	0.025(1)
O-8	0.36023(24)	0.20460(23)	0.65705(13)	0.030(1)
O-9	0.26897(21)	0.29733(20)	0.50833(13)	0.025(1)
C-1	0.14177(31)	−0.06934(28)	0.56897(18)	0.020(2)
C-2	−0.04964(34)	−0.12031(29)	0.54713(17)	0.021(2)
C-3	−0.18627(34)	−0.08034(29)	0.61712(17)	0.021(2)
C-4	−0.11864(32)	−0.11607(28)	0.70788(19)	0.021(2)
C-5	0.06865(35)	−0.05189(29)	0.72090(17)	0.022(2)
C-6	0.15141(41)	−0.08043(34)	0.80973(20)	0.033(3)
H-1	0.224(4)	−0.117(3)	0.518(2)	0.038(9)
H-2	−0.039(4)	−0.232(1)	0.544(3)	0.029(9)
H-3	−0.208(4)	0.030(1)	0.615(2)	0.023(8)
H-4	−0.095(4)	−0.226(1)	0.713(2)	0.008(6)
H-5	0.058(3)	0.059(1)	0.713(2)	0.002(6)
H-6	0.079(4)	−0.020(3)	0.858(2)	0.039(9)
H-6′	0.281(2)	−0.028(3)	0.813(2)	0.033(9)
H-22	−0.106(5)	0.026(1)	0.463(3)	0.064(13)
H-33	−0.423(4)	−0.085(3)	0.568(2)	0.041(10)
H-44	−0.268(5)	−0.144(3)	0.806(3)	0.069(13)
H-66	0.191(5)	−0.244(4)	0.885(1)	0.056(11)
H-7	0.580(3)	0.130(4)	0.505(3)	0.092(15)

[a] $U_{eq} = 1/3\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*a_ia_j$.

$P2_1$ four-circle diffractometer, Mo-K_α radiation ($\lambda = 0.71069$ Å), and a graphite monochromator were used for measurements of lattice parameters and intensities at ~ 24°. The unit-cell dimensions were obtained by a least-squares refinement of 15 reflections ($17 < 2\Theta < 22°$). More than half an Ewald sphere up to $2\Theta = 60°$ was measured by the 2Θ–ω scan technique. The intensities were corrected for Lorentz and polarisation factors only. Symmetry-related reflections among 6212 measurements were averaged to give a final set of 2487 reflections with $I > 3\sigma(I)$ which were used for the structure analysis; R_{merg} was 0.0275. Two reflections, which were monitored periodically, exhibited ±3% variation in intensity during the period of data collection. The crystal data are listed in Table I.

The structure was solved by direct methods and refined by full-matrix least-squares methods[5] minimising the function $\Sigma w(|F_o| - |F_c|)^2$, with $w = 1/\sigma^2(F_o)$, where $\sigma(F_o)$ was based on counting statistics. All hydrogen atoms were found from difference Fourier synthesis and refined with constraints $d(\mathrm{O–H}) = 0.97$ Å and $d(\mathrm{C–H}) = 1.08$ Å. The refinement yielded a final R value of 0.0326 and an R_w value of 0.0316 (refinement of the inverted structure gave $R = 0.0346$ and $R_w = 0.0340$). The non-hydrogen atoms were refined with anisotropic thermal parameters, and the hydrogen atoms with isotropic ones. In the final cycle of refinement, no parameter shifted more than 0.08 of its standard deviation. The final difference-Fourier synthesis showed maximum and minimum electron densities of -0.56 and 0.63 eÅ^{-3}, respectively. The atomic scattering factors were taken from

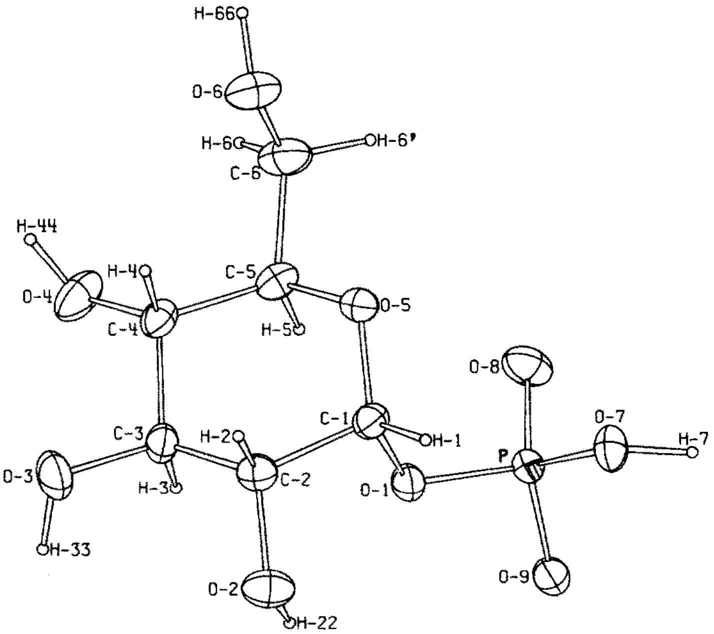

Fig. 1. The structure of the α-D-glucopyranosyl phosphate monoanion, showing the numbering of the atoms.

TABLE III

Bond lengths (Å), bond angles (°), and torsion angles (°) in the crystals of α-D-glucopyranosyl potassium hydrogenphosphate

Bond	Bond distance	Bond	Bond distance
C-1–C-2	1.527(3)	C-4–O-4	1.420(3)
C-2–C-3	1.515(4)	C-5–O-5	1.445(3)
C-3–C-4	1.509(4)	C-6–O-6	1.422(4)
C-4–C-5	1.523(4)	C-1–O-5	1.407(3)
C-5–C-6	1.509(4)	O-1–P	1.596(2)
C-1–O-1	1.423(3)	O-7–P	1.575(2)
C-2–O-2	1.416(3)	O-8–P	1.480(2)
C-3–O-3	1.434(3)	O-9–P	1.500(2)
Bonds	Bond angle	Bonds	Bond angle
O-1–C-1–C-2	106.5(2)	O-5–C-5–C-4	109.2(3)
O-1–C-1–O-5	111.6(2)	O-5–C-5–C-6	107.7(3)
C-2–C-1–O-5	111.3(3)	C-4–C-5–C-6	114.0(3)
O-2–C-2–C-1	110.7(3)	O-6–C-6–C-5	109.9(3)
O-2–C-2–C-3	112.0(3)	C-1–O-5–C-5	113.2(2)
C-1–C-2–C-3	112.0(3)	C-1–O-1–P	124.8(2)
O-3–C-3–C-2	109.6(3)	O-1–P–O-7	102.1(2)
O-3–C-3–C-4	108.8(3)	O-1–P–O-8	111.5(2)
C-2–C-3–C-4	111.6(3)	O-1–P–O-9	104.5(2)
O-4–C-4–C-3	110.0(3)	O-7–P–O-8	111.4(2)
O-4–C-4–C-5	109.0(3)	O-7–P–O-9	110.3(2)
C-3–C-4–C-5	108.9(3)	O-8–P–O-9	115.9(2)
Bonds	Torsion angle	Bonds	Torsion angle
O-7–P–O-1–C-1	39.5(4)	O-6–C-6–C-5–O-5	−64.1(4)
O-8–P–O-1–C-1	−79.6(4)	O-6–C-6–C-5–C-4	57.2(5)
O-9–P–O-1–C-1	154.4(4)	P–O-1–C-1–O-5	63.7(4)
H-7–O-7–P–O-1	167(3)	P–O-1–C-1–C-2	−174.6(5)

standard tables[6]; anomalous dispersion was included for P, K^+, O, and C atoms. The atomic positional parameters and equivalent temperature factors are listed in Table II.

DISCUSSION

The crystals of the title compound are composed of α-D-glucopyranosyl phosphate monoanions and potassium cations. The molecular configuration and conformation and the atom-numbering scheme of one anion are illustrated in Fig. 1, and the principal interatomic distances and angles are given in Table III. The conformation is $^4C_1$ with a little distortion from the ideal, having Cremer–Pople[7] puckering parameters of Q = 0.558(3) Å, Θ = 7.9(3)°, and ϕ = 297(2)°. The torsion angles O-6–C-6–C-5–O-5 and O-6–C-6–C-5–C-4 are −64.1(4) and 57.2(5)°, respectively. The conformation about the C-5–C-6 bond is therefore *gauche–gauche*. This conformation was observed[1] for $Na_2G1P \cdot 3.5H_2O$ in contrast to *gauche–trans* conformation[2] in $K_2G1P \cdot 2H_2O$.

The lengths of the endocyclic O-5–C-5 and O-5–C-1 bonds [1.445(3) and 1.407(3) Å, respectively] in the title salt are more differentiated than the corresponding lenghts in the disodium[1] and dipotassium[2] salts. The lengths of the other C–O bonds range from 1.416(3) to 1.434(3) Å and those of the C–C bonds from 1.509(4) to 1.527(4) Å, and are close to those found in other glucopyranosyl derivatives.

The length of the P–O-1 bond [1.596(2) Å] is significantly shorter than those [1.641(6) or 1.636(2) Å, respectively] in the crystals of $Na_2G1P \cdot 3.5H_2O$ (ref. 1) and $K_2G1P \cdot 2H_2O$ (ref. 2). Such differentiation is normally observed in mono- and double-ionised phosphate monoesters[8].

Comparison of the geometries of the dianions[1,2] and the monoanion reveals the largest differences in the O-5–C-1–O-1–P fragment. The lengths of the O-5–C-1 and O-1–C-1 bonds in the dianions approach the standard values according to the classification of Tvaroška and Bleha[9]. In the monoanion, the length of the

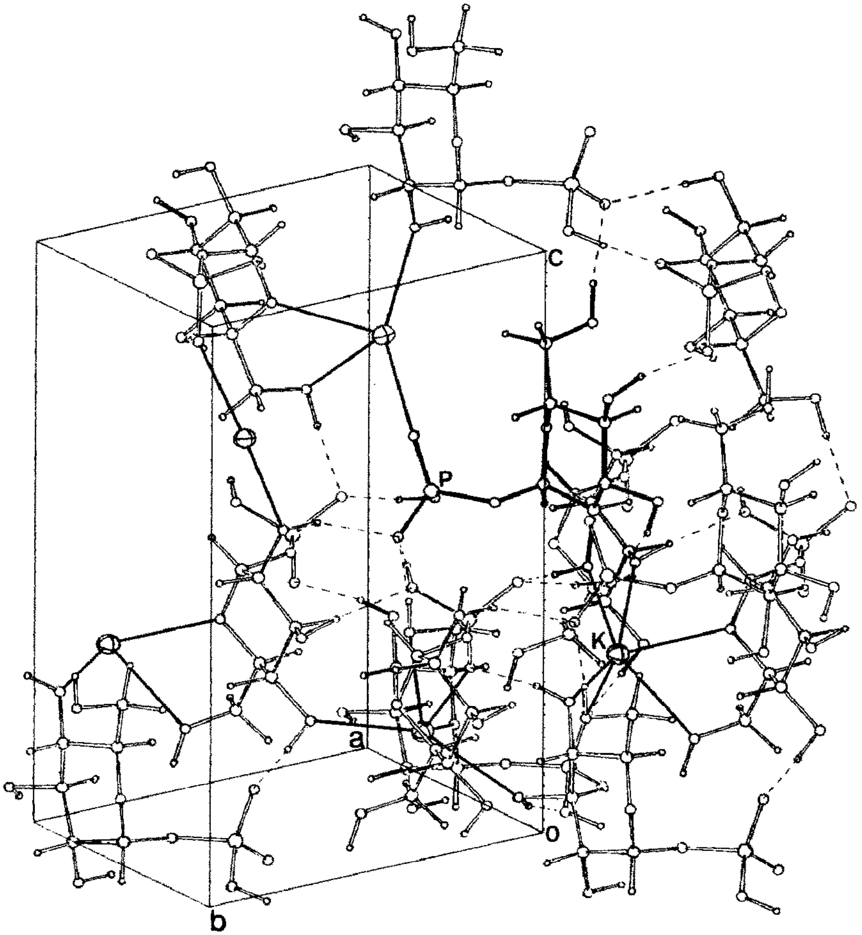

Fig. 2. The packing in the crystal of α-D-glucopyranosyl potassium hydrogenphosphate.

TABLE IV

Hydrogen bond distances (Å) and angles (°) in the crystal of α-D-glucopyranosyl potassium hydrogenphosphate

O-H···O	O···O	H···O	O-H···O
O-2–H-22···O-9^{a}	2.873(3)	1.99(3)	150(3)
O-2–H-22···O-1	2.719(3)	2.36(4)	101(3)
O-3–H-33···O-7^{b}	2.917(3)	1.97(3)	166(3)
O-4–H-44···O-8^{c}	2.651(3)	1.70(3)	165(3)
O-6–H-66···O-9^{d}	2.938(3)	1.97(2)	174(3)
O-7–H-7···O-9^{e}	2.539(3)	1.57(3)	174(4)

Symmetry codes: ^{a} $x-0.5,\ 0.5-y,\ 1-z$; ^{b} $x-1,\ y,\ z$; ^{c} $-x,\ y-0.5,\ 1.5-z$; ^{d} $0.5-x,\ -y,\ 0.5+z$; ^{e} $0.5+x,\ 0.5-y,\ 1-z$.

C-1–O-5 bond of 1.407(3) Å is significantly shorter than the standard value (1.422 Å), and that of the O-1–C-1 bond length of 1.423(3) Å is significantly longer than the standard value of 1.400 Å.

The conformation about the P–O-1 bond accords with the common conformation about the phosphate bond in phosphate monoesters, i.e., one of the terminal phosphate oxygens is *trans* to C-1 and involves the smallest O(ester)–P–O bond angle.

The crystal packing and hydrogen bonding schemes are shown in Fig. 2. All of the hydroxyl hydrogen atoms participate in hydrogen bonding. The hydrogen-bond lengths and angles are listed in Table IV *.

TABLE V

Potassium co-ordination distances (Å) and angles (°) in the crystal of α-D-glucopyranosyl potassium hydrogenphosphate

Bond	Bond distance	Bond	Bond distance
K–O-2	2.753(2)	K–O-5^{c}	2.780(2)
K–O-3^{a}	2.806(2)	K–O-6^{c}	2.774(2)
K–O-4^{b}	2.713(2)	K–O-8^{d}	2.660(2)
Bonds	**Bond angle**	**Bonds**	**Bond angle**
O-2–K–O-3^{a}	74.5(1)	O-3^{a}–K–O-8^{d}	91.8(1)
O-2–K–O-4^{b}	76.7(1)	O-4^{b}–K–O-5^{c}	112.5(1)
O-2–K–O-5^{c}	89.1(1)	O-4^{b}–K–O-6^{c}	82.3(1)
O-2–K–O-6^{c}	133.1(1)	O-4^{b}–K–O-8^{d}	105.9(1)
O-2–K–O-8^{d}	143.6(1)	O-5^{c}–K–O-6^{c}	61.2(1)
O-3^{a}–K–O-4^{b}	148.7(1)	O-5^{c}–K–O-8^{d}	120.9(1)
O-3^{a}–K–O-5^{c}	76.6(1)	O-6^{c}–K–O-8^{d}	82.4(1)
O-3^{a}–K–O-6^{c}	125.0(1)		

Symmetry codes: ^{a} $0.5+x,\ -0.5-y,\ 1-z$; ^{b} $-0.5-x,\ -y,\ z-0.5$; ^{c} $x-0.5,\ -0.5-y,\ 1-z$; ^{d} $0.5-x,\ -y,\ z-0.5$.

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* Tables of the final anisotropic thermal parameters, and observed and calculated structure factors have been deposited with, and can be obtained from, Elsevier Scientific Publishing Company, BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/497/Carbohydr. Res., 229 (1992) 33–39.

The K^+, which is six co-ordinated [at distances 2.660(2)–2.806(2) Å] by five sugar and one phosphate oxygen atoms (Table V), binds to five independent α-D-glucopyranose moieties, each of which chelates to the K^+ as a bidendate ligand involving O-5,6.

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