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The Crystal Structure of a Naturally Occurring γ -Lactone Glucoside ($C_{11}H_{16}O_8 \cdot H_2O$) from *Helleborus Foetida* L.

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The crystal structure of the title compound has been determined. The cell is monoclinic, space group $P2_1$ with $Z=2$. Cell parameters are $a=11.41(2)$, $b=10.82(2)$, $c=5.33(2)$ Å, $\beta=95.72(6)^\circ$. All reflexions with $l>0$ and $2\theta \leq 52^\circ$ (1280 independent) were measured using a four-circle diffractometer equipped with a crystal monochromator and a scintillation counter. Mo $K\alpha$ radiation was employed. The structure was determined by the symbolic addition method and was refined by the least-squares method to a final R value of 0.051 using 1161 independent reflexions considered to be observable. The compound contains a β -glucose unit fused to a dioxane ring, onto which a γ -lactone ring is attached in spiro arrangement.

Introduction

The compound studied was isolated by Dr E. Wollenweber at the Botanical Institute of the Technical University of Darmstadt, and a sample was sent to Dr J. Lam of this department for chemical investigations. We undertook a crystallographic study, and at the time we determined the structure, a paper was published (Tschesche, Welmar, Wulff & Snatzke, 1972) describing a compound which appeared to be the same and proposing a structure which was qualitatively equivalent to the one which we had arrived at, except that the stereochemistry at C(4') (Fig. 1) could not be

obtained by the methods used by Tschesche *et al.* Professor Tschesche kindly sent us a sample of the crystal isolated in his laboratory, and rotation and Weissenberg X-ray photographs of his and of our samples were completely identical as regards both lattice spacings and relative intensities. A preliminary communication was published (Mariezcurrana, Rasmussen, Lam & Wollenweber, 1972), emphasizing the stereochemistry at C(4'). This paper communicates details about the structure solution and quantitative details about bond lengths *etc.*

Experimental

Crystals were kindly supplied by Dr Wollenweber, Botanical Institute, Technical University of Darmstadt, through Dr J. Lam, Department of Organic

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Table 1. *Statistically expected values*

	Av. $ E $	Av. $ E^2 - 1 $	Av. $ E^2 $	% $ E > 1$	% $ E > 2$	% $ E > 3$
Centro.	0.798	0.968	1.00	32.0	5.0	0.3
Non-centro.	0.886	0.736	1.00	36.8	1.8	0.01
Glucoside	0.864	0.843	1.03	33.1	3.8	0.4

Chemistry at Aarhus University. A crystal of dimensions $0.2 \times 0.3 \times 0.4$ mm was mounted along the c axis. Weissenberg and precession photographs were taken to establish the crystal system and systematic absences. A test for piezoelectricity was positive and solutions of the compound exhibited optical activity. The reflexions $0k0$ were systematically absent for k odd, and the crystals were monoclinic. The combined evidence favours the space group $P2_1$. The density was measured by flotation in a solution of carbon tetrachloride and heptane.

Crystal data

Monoclinic, space group $P2_1$, $a = 11.41$ (2), $b = 10.82$ (2), $c = 5.33$ (2) Å, $\beta = 95.72$ (6)°, $V = 651$ Å³, Formula (C₁₁H₁₆O · H₂O), F.W. 294.1, $D_m = 1.495$, $D_c = 1.493$ g cm⁻³, $Z = 2$, $\mu(\text{Mo } K\alpha) = 1.6$ cm⁻¹, $\lambda = 0.7107$ Å.

Intensities were measured on a Picker computer-controlled four-circle diffractometer. A monochromator constructed in this department was employed using pyrolytic graphite to select Mo $K\alpha$ radiation. Harmonics were suppressed by setting the pulse height analyser to about 99% transmission of the desired wavelength.

The moving-crystal, moving-counter technique (θ - 2θ scan) was used. Background was estimated by stationary counting at $\pm 0.8^\circ 2\theta$ from the peak maxima. The scan speed was 1° min^{-1} . The estimated standard deviation $\sigma_s(F_o^2)$ is based on counting statistics.

The crystal was mounted with the c axis parallel to the φ axis of the instrument.

As a check on the stability of both the crystal and the electronic equipment, three reflexions were measured every 30 reflexions throughout the data collection period. No significant fluctuations were observed. Of the 1280 independent reflexions 120 have $F^2 < 2 \times \sigma(F_o^2)$ and were considered unobserved. No absorption correction was applied.

Solution and refinement

The structure was solved by direct methods using the symbolic addition method and the tangent refinement procedure. A CDC6400 version of the program *SYMBAD* was used. A Wilson plot was used for obtaining an average temperature factor and scale factor.

Table 1 shows the statistically expected values, and Table 2 the distribution for the different parity groups.

The physical tests for absence of a centre of symmetry were more conclusive in this case than the statistical test.

Table 2. *Average $|E^2|$ for parity groups*

	Av. $ E^2 $	Number of reflexions
<i>ggg</i>	1.074	179
<i>ggu</i>	0.987	169
<i>gug</i>	1.018	153
<i>guu</i>	1.179	148
<i>ugg</i>	1.027	171
<i>ugu</i>	1.061	160
<i>uug</i>	0.979	142
<i>uuu</i>	0.938	139

From the 1161 reflexions, 417 with $E > 1.0$ were used for the phase determination. The starting set is given in Table 3.

Table 3. *Starting set*

h	k	l	E	Phases
-7	0	4	3.46	0
-5	0	-1	2.81	0
-6	-1	3	2.41	0
-1	-2	1	3.11	a
7	-5	2	3.41	b
8	-5	1	2.50	c
3	-3	3	2.36	d
2	-6	4	2.91	$-\pi/2$ enantiomorph
$\bar{6}$	0	4	3.22	0

The initial symbolic addition procedure was carried out by hand, and one possible set $a = \pi$, $b = c = d = 0$ was expanded by tangent refinement giving phases of 402 reflexions after 10 cycles. From the first E map 8 peaks which could be fitted to a chemical structure were chosen. The first structure-factor calculation gave an $R = 50\%$.

Phases were computed from the partial structure and those phases for which there was an agreement between the largest computed and observed structure factors were accepted to form a basic set for expansion by the tangent formula (Karle, 1968).

By repeated application of this procedure all the carbon and oxygen atoms were found in successive Fourier maps. The positional and isotropic thermal parameters of these atoms were refined by full-matrix three-dimensional least-squares computations using unit weights. After three cycles an R value of 0.101 was obtained. Anisotropic thermal parameters were now assigned to all atoms and after three cycles of refinement R was reduced to 0.082.

Hydrogen atoms were located from a difference Fourier map computed using only reflexions with $\sin \theta / \lambda < 0.35$ Å⁻¹. This map showed 16 hydrogen atoms. A new difference Fourier map showed the two additional hydrogen atoms.

Refinement was continued including all atoms in the computation. For the heavy atoms anisotropic temperature factors were used, and isotropic temperature factors were applied for the hydrogen atoms. An isotropic extinction correction was employed and therefore an extinction parameter (Zachariasen, 1967) was applied. The lowest value of the extinction correction applied to the calculated structure factor was 0.92, and the extinction factor was 4.10×10^{-6} . Weights were chosen as $w = 1/\sigma^2(F_o)$ with $\sigma(F_o) = [\sigma_s(F_o^2) + kF_o^2]^{1/2} - |F_o|$ where $\sigma_s(F_o^2)$ is derived from counting statistics. Weights were adjusted after each cycle of refinement by changing k , so that $\langle w|F_o - F_{calc}| \rangle$ varied as little as possible with the magnitude of F_o .

The value of k for the last cycle was 1.06. The final values of the usual measures of goodness-of-fit are as follows: Conventional R index is $R = 0.051$ and the corresponding weighted value is $R_w = 0.064$.

In the last cycle of refinement the maximum coordinate shift for non-hydrogen atoms was 0.1 σ and for the hydrogen atoms 0.4 σ . The standard deviation of an observation of unit weight was 0.99.

A final difference electron density map calculated with both heavy atoms and hydrogen atoms included in the values for the calculated structure factors showed no peaks exceeding 0.7 e \AA^{-3} in magnitude. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962) for the heavy atoms, and for hydrogen atoms the contracted hydrogen

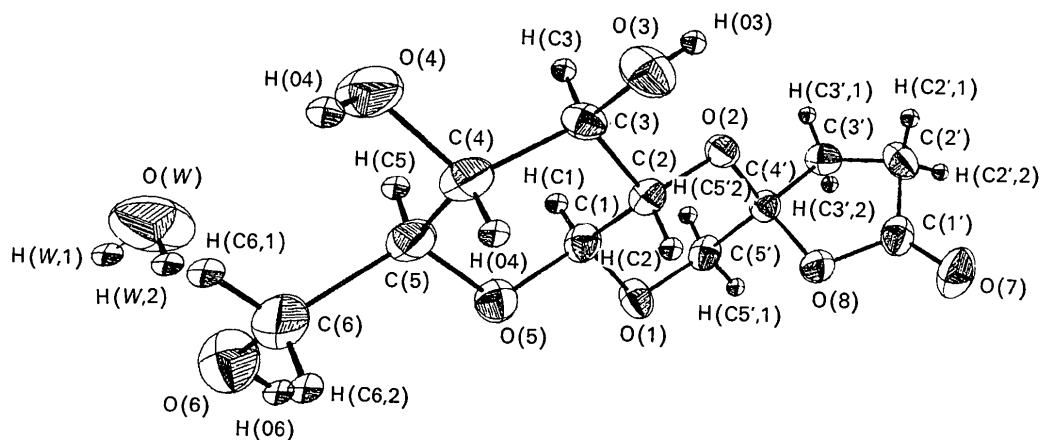


Fig. 1. Perspective drawing of a glucoside molecule. The thermal vibration ellipsoids are shown on a 50% probability scale. The β -glucoside unit is drawn arbitrarily in the L-configuration.

Table 4. Fractional coordinates

All coordinates are $\times 10^5$.

(a) Non-hydrogen atoms.

Thermal parameters, U^{ij} ($\text{\AA}^2 \times 10^4$), are as they appear in the Debye-Waller expression: $\exp(-2\pi^2 a_i^* a_j^* h_i h_j U^{ij})$, e.s.d.'s in the last significant figure are in parentheses.

	x/a	y/b	z/c	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O(5)	2074 (30)	84157 (39)	1292 (62)	275 (18)	295 (20)	367 (23)	-15 (12)	-9 (10)	59 (12)
C(5)	-6976 (28)	77531 (48)	12480 (58)	301 (19)	308 (84)	280 (23)	-38 (15)	65 (10)	-20 (12)
C(4)	-2353 (32)	64868 (36)	22319 (56)	316 (21)	304 (22)	287 (20)	-48 (18)	59 (16)	-30 (10)
O(4)	-11160 (30)	58755 (38)	34635 (58)	393 (25)	419 (22)	327 (23)	-186 (20)	43 (20)	-10 (20)
O(3)	13369 (30)	54465 (37)	46989 (65)	442 (20)	267 (21)	448 (18)	-28 (16)	-53 (15)	83 (16)
O(2)	27375 (25)	76784 (33)	45711 (53)	268 (18)	309 (20)	273 (21)	-18 (16)	-43 (16)	51 (16)
C(3)	8747 (40)	66327 (94)	40871 (76)	314 (21)	266 (20)	230 (18)	-34 (16)	-26 (15)	2 (10)
C(4')	35628 (38)	84363 (43)	35297 (69)	249 (24)	272 (23)	301 (20)	-19 (16)	18 (15)	16 (15)
C(2)	17370 (37)	74327 (43)	28313 (70)	252 (23)	232 (25)	272 (24)	-21 (15)	44 (16)	-21 (16)
C(5')	29977 (40)	96012 (46)	23516 (89)	298 (26)	261 (25)	408 (25)	-27 (14)	85 (16)	56 (16)
C(1)	11656 (38)	86319 (45)	19183 (80)	250 (26)	279 (25)	365 (23)	-30 (16)	39 (16)	28 (16)
O(6)	-22420 (30)	87767 (41)	-14681 (73)	349 (20)	414 (21)	580 (22)	-12 (16)	-43 (16)	82 (15)
O(8)	40580 (28)	77331 (38)	15430 (54)	317 (18)	370 (18)	268 (14)	42 (14)	38 (14)	-28 (13)
C(6)	-17253 (39)	76198 (43)	-7791 (77)	270 (26)	364 (28)	372 (23)	89 (20)	20 (18)	-25 (21)
O(1)	19747 (27)	93358 (37)	6711 (63)	250 (17)	321 (19)	440 (18)	-28 (12)	-51 (13)	14 (14)
O(7)	55384 (35)	64470 (44)	12249 (71)	569 (27)	560 (25)	634 (26)	188 (20)	186 (20)	-101 (20)
O(W)	-33481 (38)	1524 (40)	19497 (78)	699 (30)	732 (31)	537 (24)	213 (22)	-26 (22)	-15 (22)
C(31)	45933 (42)	86713 (43)	54917 (78)	354 (28)	388 (28)	314 (23)	-100 (20)	-8 (18)	-18 (19)
C(2')	54177 (42)	76044 (96)	51253 (89)	370 (31)	465 (31)	437 (27)	11 (23)	-84 (23)	82 (22)
C(1')	50637 (43)	71763 (50)	24827 (80)	328 (29)	281 (25)	479 (27)	23 (19)	99 (21)	70 (20)

Table 4 (cont.)

(b) Hydrogen atoms.

All coordinates are $\times 10^4$ and U_{iso} 's $\times 10^3$.

	x/a	y/b	z/c	U_{iso}
H(C2',1)	5310 (38)	6951 (46)	6077 (86)	36 (11)
H(C2',2)	6247 (52)	7852 (65)	5135 (90)	73 (18)
H(C3',1)	4333 (42)	8649 (53)	6935 (90)	25 (14)
H(C3',2)	4988 (37)	9408 (38)	5072 (83)	19 (9)
H(C5',1)	3574 (31)	32 (36)	1464 (69)	6 (9)
H(C5',2)	2856 (35)	41 (44)	3727 (83)	23 (12)
H(C1)	858 (31)	9074 (34)	3197 (69)	10 (8)
H(C2)	1943 (37)	7070 (43)	1390 (84)	31 (11)
H(O3)	1843 (46)	5527 (45)	5775 (84)	50 (15)
H(C3)	694 (34)	7068 (39)	5727 (81)	21 (10)
H(C4)	26 (30)	6078 (39)	926 (70)	6 (9)
H(C5)	-938 (40)	8249 (44)	2652 (82)	26 (11)
H(C6,1)	-2317 (33)	7142 (39)	16 (79)	19 (10)
H(C6,2)	-1455 (43)	7250 (48)	-2120 (90)	36 (15)
H(O6)	-1854 (49)	9227 (62)	-2107 (99)	44 (18)
H(O4)	-1382 (35)	5335 (40)	2583 (80)	30 (11)
H(W,1)	-3032 (49)	9677 (61)	842 (90)	64 (17)
H(W,2)	-3801 (67)	704 (86)	1235 (99)	70 (28)

atom scattering factors reported by Stewart, Davidson & Simpson (1965) were used. Table 4 shows the coor-

dinates and the thermal parameters obtained by the least-squares refinement. A table of observed and calculated structure factors. is available.*

Discussion of the molecular structure

The identification of the atoms and an illustration of the 50% probability thermal ellipsoids are shown in Fig. 1. The unit-cell contents are shown in Fig. 2.

The molecule contains a β -glucose unit fused onto a dioxane ring. A saturated γ -lactone ring is connected to the dioxane ring in a *spiro* arrangement. The γ -lactone ring deviates significantly from planarity (Table 5); however, the C(2')-C(1')-O(8) group is planar.



* This table has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30058. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

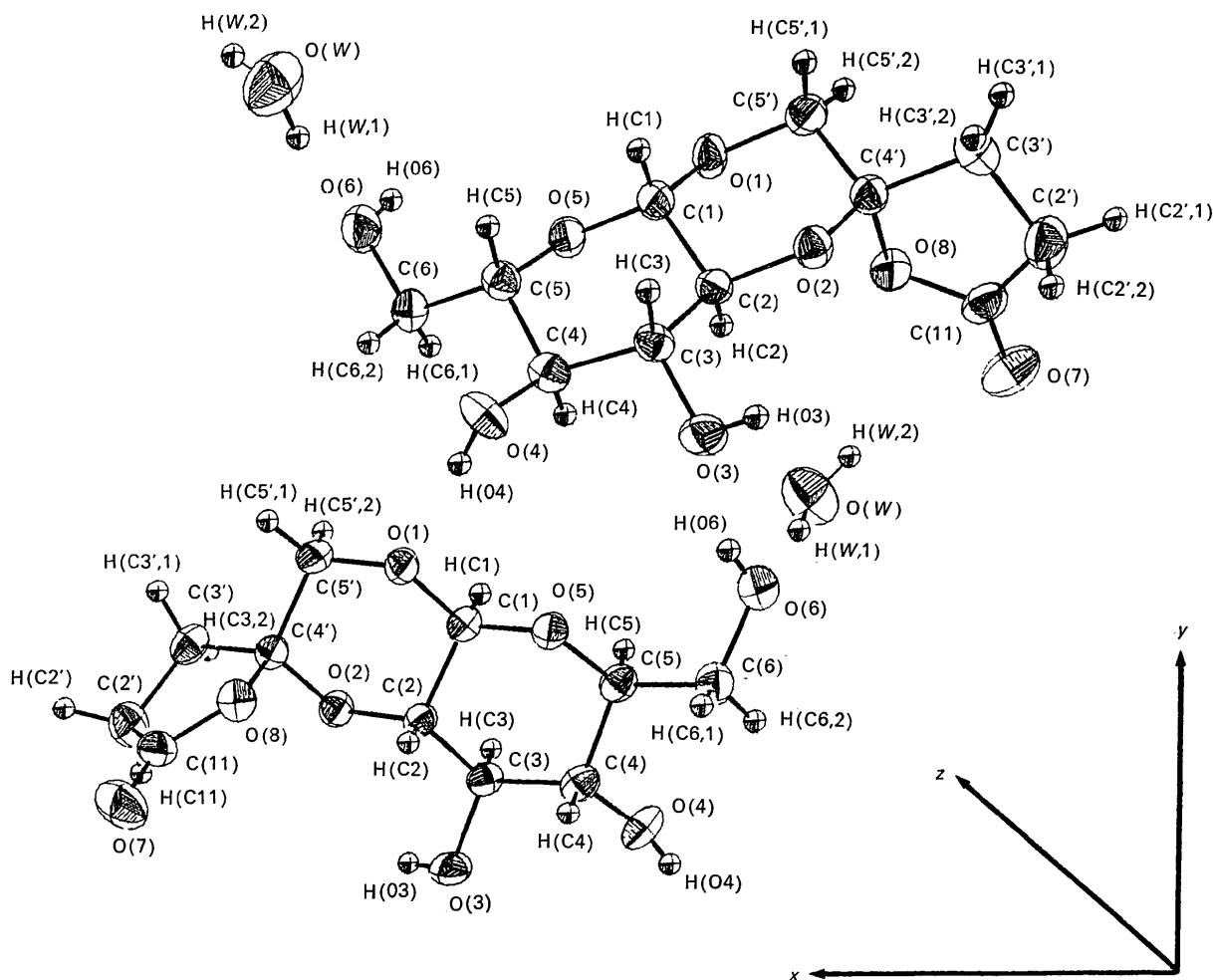


Fig. 2. The content of a unit cell shown in relation to the axes.

Table 5. *Least-squares plane through C—CO₂ group*

The plane is of the form $AX + BY + CZ - D = 0$.
 $A = 6.5023$, $B = 8.0249$, $C = -2.1797$, $D = 8.5086$.

Distances of atoms in the γ -lactone group from plane

O(7)	-0.0007 Å
O(8)	-0.0005
C(2')	-0.0005
C(1')	0.0017
C(4')	-0.191
C(3')	0.239

This is in agreement with results reported by Jeffrey & Kim (1966) concerning the lactone group in a glucuronolactone compound.

The two carbon-oxygen bond lengths of the O(8) oxygen atom in the γ -lactone ring differ significantly. The O(8)—C(1') bond of 1.35 Å approaches the normal C—OH bond length of 1.31 Å in carboxylic acid groups. The O(8)—C(4') bond of 1.46 Å is significantly larger than the average C—OH single bond length (1.41 Å) found elsewhere in the structure. This difference between the two oxygen-carbon bonds correlates well with the fact that the γ -lactone ring is fairly easily opened by hydrolysis.

Table 6. *Bond lengths*

E.s.d.'s are shown in parentheses.

C(5)—C(4)	1.542 (2) Å
C(4)—C(3)	1.535 (4)
C(3)—C(2)	1.515 (6)
C(2)—C(1)	1.515 (6)
C(1)—O(5)	1.397 (4)
O(5)—C(5)	1.435 (3)
C(5)—C(6)	1.520 (5)
C(6)—O(6)	1.417 (6)
C(4)—O(4)	1.417 (3)
C(3)—O(3)	1.414 (6)
C(2)—O(2)	1.422 (5)
O(2)—C(4')	1.404 (5)
C(4')—C(5')	1.523 (6)
C(5')—O(1)	1.427 (6)
O(1)—C(1)	1.413 (5)
C(4')—C(3')	1.515 (6)
C(3')—C(2')	1.514 (7)
C(2')—C(1')	1.499 (7)
C(1')—O(8)	1.347 (6)
O(8)—C(4')	1.462 (5)
C(1')—O(7)	1.200 (6)
H(O4)—O(4)	0.82 (6)
H(O6)—O(6)	0.80 (4)
H(O3)—O(3)	0.79 (6)
H(C4)—C(4)	0.92 (7)
H(C3)—C(3)	1.02 (4)
H(C2)—C(2)	0.91 (5)
H(C1)—C(1)	0.93 (4)
H(C5',1)—C(5')	0.98 (7)
H(C5',2)—C(5')	0.91 (7)
H(C3',1)—C(3')	0.88 (6)
H(C3',2)—C(3')	0.95 (4)
H(C2',1)—C(2')	0.89 (4)
H(C2',2)—C(2')	0.98 (7)
H(W,1)—O(W)	0.89 (6)
H(W,2)—O(W)	0.86 (6)

The other bond lengths in the molecule are close to values commonly found in chemically related compounds. Tables 6 and 7 list bond lengths and bond angles.

Table 7. *Bond angles*

Numbers in parentheses are standard deviations.

C(5)—C(6)—O(6)	111.8 (4)°
C(6)—O(6)—H(6)	116.0 (4)
O(5)—C(5)—C(4)	110.5 (4)
C(5)—C(4)—C(3)	111.1 (2)
C(3)—C(2)—C(1)	110.8 (3)
C(2)—C(1)—O(5)	111.0 (3)
C(1)—O(5)—C(5)	110.3 (2)
C(4)—O(4)—H(O4)	108.6 (3)
C(3)—O(3)—H(O3)	107.5 (4)
C(2)—O(2)—C(4')	112.2 (3)
O(2)—C(4')—C(5')	111.9 (3)
C(4')—C(5')—O(1)	112.2 (3)
C(5')—O(1)—C(1)	110.2 (3)
O(1)—C(1)—C(2)	109.5 (3)
C(1)—C(2)—O(2)	110.0 (3)
C(4')—C(3')—C(2')	103.4 (4)
C(3')—C(2')—C(1')	104.1 (4)
C(2')—C(1')—O(8)	110.5 (4)
C(1')—O(8)—C(4')	110.0 (3)
C(2')—C(1')—O(7)	129.3 (5)
H1(W)—O(W)—H2(W)	112.0 (5)

The water molecule links two glucoside molecules through hydrogen bonding. More hydrogen bonds are established between hydroxyl groups. The more important bonds are indicated in Table 8.

Table 8. *Hydrogen bonds*

Atom A	-H...	Atom B	A-B	H...B
O(W)	H(W,1)	O(6)	2.754 Å	1.87 Å
O(W)	H(W,2)	O(7 ⁱ)	3.198	2.40
O(3)	H(O3)	$\frac{1}{2}bO(W^i)$	2.781	2.04
O(4)	H(O4)	$-bO(1^i)$	2.856	2.09
O(6)	H(O6)	O(3)	2.766	2.04

The labelling scheme for symmetry-related atoms is

Coordinates	Superscript
x, y, z	None
$\bar{x}, \frac{1}{2} + y, \bar{z}$	i

A symbol such as $+aO(7^i)$ indicates the symmetry-related atom O(7ⁱ) displaced by a translation $+a$ and so on.

Computation

All calculations were carried out on a CDC6400 computer at the Computing Center of Aarhus University. The following programs were used:

Data reduction: *DRAM* 1 (Lehmann, 1970).
 Direct methods: *SYMBAD* (Danielsen, 1971).
 Fourier synthesis: *FORDAP* (A. Zalkin, modified by Lundgren and Liminga).
 Least-squares refinement: *LINUS*, modification of *ORFLS* (Busing, Martin & Levy, 1962) by W. C. Hamilton, J. A. Ibers and J. Edmonds.
 Ellipsoid plot program: *ORTEP* (Johnson, 1965).

Distance and angle program: *ORFFE* (Busing, Martin & Levy, 1964)

The last three programs were used from the SUNY Buffalo crystallographic computer programs, a system developed under the guidance of P. Coppens.

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The Crystal Structure of Potassium Boromate ($\text{KBC}_8\text{H}_8\text{O}_{10}\cdot\text{H}_2\text{O}$)

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The crystal and molecular structure of the title compound has been determined by X-ray diffraction techniques. The space group is $P2_1$, with two formula units per unit cell. The cell parameters are $a = 5.54$ (2), $b = 11.98$ (2), $c = 10.74$ (2) Å, $\beta = 113.2$ (5)°. Intensities h, k, l , $k = 0$ to 14, were measured using a linear diffractometer equipped with a crystal monochromator and a scintillation counter. 1680 independent reflexions were obtained. The structure was solved by direct methods combined with Patterson methods and chemical knowledge. It was refined by full-matrix least-squares methods to a final R value of 0.056 using 1638 independent reflexions considered to be observable. The two malate groups showed differences in the thermal parameters and in bond lengths. A refinement constraining the two malate groups to have identical geometry gave an R value of 0.087, and confirmed the differences in the thermal parameters. The potassium and the boron atoms are coordinated to oxygen atoms of the carboxyl and hydroxyl groups. The boron atom is tetrahedrally coordinated, and the potassium atom exhibits five-coordination.

Introduction

The acidity of orthoboric acid, $\text{B}(\text{OH})_3$, is greatly increased by the addition of polyhydroxy compounds like glycerol, mannitol, *etc.* through the formation of complex compounds. Studies of acid–base equilibria and of electrolytic conductance have confirmed the existence of negative complex ions containing boron. Few such crystalline compounds have been characterized and to our knowledge only one, boromycin, has

been subjected to X-ray structure analysis (Dunitz, Hawley, Mikloš, White, Berlin, Marušić & Prelog, 1971). The classical work of Böeseken and his collaborators showed that α -hydroxy-acids can also take part in complex formation with boric acid, and potassium boromate is one of the few crystalline complexes of boron with hydroxyl compounds which has been reported. It is described in a paper by Jones (1933) and we obtained crystals suitable for X-ray crystallography by following his procedure.

The aim of our investigation was the determination of the geometry of a boric acid complex and the study of boron–oxygen distances in a compound of this kind.

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