fluorocitrate when it chelates to the enzyme-bound ferrous iron in a manner similar to that of isocitrate.

The inactivation of aconitase with time is more complicated. It has been suggested that it is possibly due to alkylation at the active site following, for instance, cleavage of the C–F bond (Kun, 1969; Carrell et al., 1970). Alternatively the central carboxyl group of fluorocitrate may hydrogen-bond to the hydrogen abstracting site. Further biochemical studies on this problem and on the effect of fluorocitrate on the tricarboxylate carrier of mitochondria (Eanes et al., 1972) are now in progress in various laboratories.

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The Crystal Structure of Lithium Formate Monohydrate

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The structure of $LiHCOO.H_2O$ has been determined. The space group is $Pbn2_1$ with 4 molecules per unit cell. 1027 Mo $K\alpha$ reflexions gave a final R value of 4·9%. All hydrogen atoms were found.

Introduction

Though crystallographic data for lithium formate monohydrate were published long ago (Nitta, 1928), the structure was not known. Raman studies with polarized light (Cadène, 1970) suggested a tetrahedrally coordinated Li ion and formate ions in planes parallel to (100), forming hydrogen bonds 2·74 Å long. This is confirmed by the present work.

Experimental

Lithium formate was prepared by neutralizing a solution of formic acid in water with lithium carbonate. After several days, long transparent needles separated from the solution. By cutting and etching with water a crystal approximately $0·3 \times 0·3 \times 0·4$ mm was obtained and sealed in a Lindemann-glass capillary tube to protect it from moisture. Data were collected on a Nonius automatic diffractometer at 20°C, using Zr-filtered Mo $K\alpha$ radiation. 1027 reflexions with $\theta < 40°$ were measured using the $\theta/2\theta$ scanning technique; 166 had an intensity smaller than twice the standard deviation as estimated from counting statistics. The crystal was rotated about [001].

The systematic absences were: $0kl$ with $k = 2n + 1$; $h0l$ with $h + l = 2n + 1$, indicating the space group

Table 1. *Positional and thermal parameters*

All U values are given in Å^2. Standard deviations in the last digits are shown in parentheses.

(*a*) Heavy atoms

Values are $\times 10^4$. The anisotropic temperature factor used was

$$\exp\left[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23}\right].$$

	X/a	Y/b	Z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C	3876 (2)	3046 (1)	172 (3)	375 (6)	222 (4)	223 (4)	−26 (4)	−22 (5)	−26 (4)
O(1)	4001	2920	2719	579	231	222	− 3	− 1	27
O(2)	4220	4098	−1145	385	291	217	−61	−41	44
O(3)	3893	340	4500 (0)	328	259	306	− 6	−21	43
Li	3844 (3)	4509 (2)	5012 (5)	346 (8)	268 (8)	236 (9)	11 (7)	−18 (8)	26 (7)

Table 1 (*cont.*)

(*b*) Hydrogen atoms

Values are $\times 10^3$, except for those for B, which are $\times 1$.

The isotropic temperature factor was

$$\exp\left(-8\pi^2 U \sin^2 \theta/\lambda^2\right)=\exp\left(-B\sin^2\theta/\lambda^2\right).$$

	X/a	Y/b	Z/c	U	B
H(1)	346 (2)	232 (2)	−71	41 (4)	3·2 (3)
H(2)	395	119	413	56 (5)	4·4 (4)
H(3)	454	30	578	31 (4)	2·4 (3)

Pbnm or *Pbn*2$_1$. As lithium formate is piezoelectric, the space group has to be *Pbn*2$_1$. The unit cell contains 4 molecules (Nitta, 1928); the dimensions are: $a=6\cdot483$ (4); $b=9\cdot973$ (7); $c=4\cdot847$ (5) Å.

Structure determination

A three-dimensional sharpened Patterson synthesis gave the coordinates of the carbon and oxygen atoms. After several cycles of refinement of positional and

Table 2. *Observed and calculated structure factors* ($\times 10$)

isotropic temperature parameters a difference Fourier synthesis revealed the position of the Li ion. After further refinement with anisotropic temperature factors a second difference-Fourier map was calculated which showed the positions of the H atoms. Refinement was carried out with a modification of the program *ORFLS* (Busing, Martin & Levy, 1962). Atomic scattering factors for carbon and oxygen atoms were calculated (Harkema, 1971) from the atomic wave functions of Clementi (1965). The scattering factor for hydrogen was taken from Stewart, Davidson & Simpson (1965), and that for Li$^+$ from Hurst, Miller & Matsen (1958).

In the last stage of refinement a correction for secondary extinction was applied (Larson, 1969). As the linear absorption coefficient for Mo radiation was 1·55 cm^{-1}, no absorption correction was applied. The final *R* index was 4·9%. Positional and thermal parameters are given in Table 1. Structure factors are given in Table 2.

Discussion of the results

The most important bond distances and angles are given in Table 3.

Table 3. *Bond distances* (Å) *and angles* (°) *with standard deviations in parentheses*

C —O(1)	1·244 (3)
C —O(2)	1·248 (3)
C —H(1)	0·88 (3)
O(1)···O(3)	2·715 (3)
O(3)···O(3″)	2·897 (3)
O(1)—C —O(2)	125·5 (2)
O(1)—C —H(1)	115 (2)
O(2)—C —H(1)	120 (2)
O(3)—H(2)···O(1)	170 (3)

Li tetrahedron

Li–O(2′)	1·923 (4)
Li–O(2″)	1·954
Li–O(1)	1·938
Li–O(3‴)	1·974

The lithium ion (Fig. 1) is tetrahedrally coordinated with 3 formate oxygens and one water oxygen. The angles vary between 104 and 112°, the Li–O distances between 1·923 and 1·974 Å, comparable with *e.g.* 1·89–2·04 Å in lithium acetate dihydrate (Galigné, Mouvet & Falgueirettes, 1970) and 1·935–2·076 Å in lithium oxalate (Beagley & Small, 1964). The water molecules form infinite zigzag chains parallel to the *c* axis, with hydrogen bonds of 2·897 Å, while the other water hydrogen atom forms a link with the formate ion. Muthukrishnan & Ramakrishna (1971) concluded from n.m.r. data that H(3) should be disordered, occupying two potential minima between 2 water oxygen atoms. Our data, however, indicate complete localization of H(3).

The formate group is probably planar: the distance of the H atom from the plane of the C and O atoms
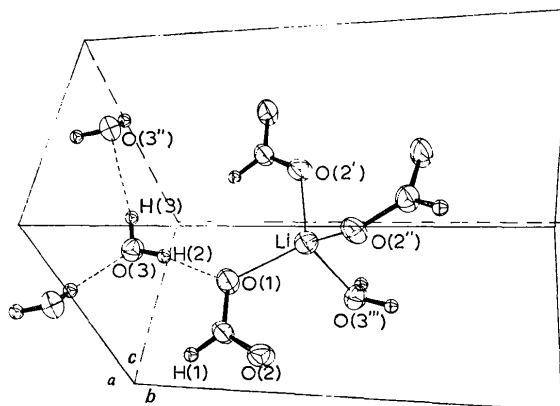

Fig. 1. Arrangement of some molecules in the unit cell, showing the coordination of the Li ion and the water chain.

is 0·03 Å, comparable to the standard deviation. When our refinement was completed, we received the paper of Mohana Rao & Viswamitra (1971), who had also determined the structure of lithium formate monohydrate from 331 Cu *K*α reflexions with film methods. Their results agree reasonably with ours (though theirs are, of course, less accurate). Contrary to our results, however, they found a significant difference in the C–O bond lengths, C–O(1) = 1·213(12); C–O(2) = 1·279(12) Å, which they explained by the different environments of the two oxygen atoms. Indeed O(2) is coordinated to two Li ions, O(1) only to one, but it forms the hydrogen bond. The infrared (Harvey, Morrow & Shurvell, 1963; Donaldson, Knifton & Ross, 1964) and Raman (Ramanujam, 1969; Cadène, 1970) spectra show a slight splitting of some fundamentals, but the splitting is very small (< 20 cm^{-1}) and each of the four spectra gives a different result. Our conclusion is that the effect of the hydrogen bond compensates for the loss of a Li coordination, so both bonds should be approximately equal.

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The Crystal Structure of 5-Bromo-12S-tetrahydroaustamide
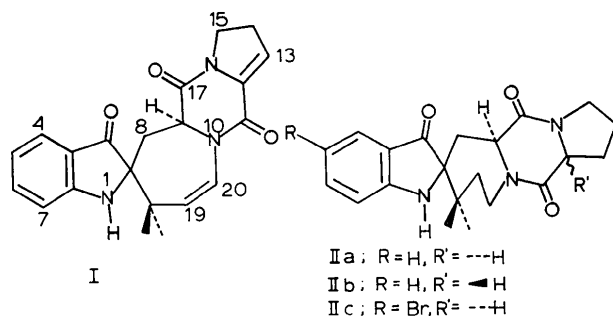
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The crystal structure of 5-bromo-12S-tetrahydroaustamide has been determined by three-dimensional X-ray analysis. The crystals are monoclinic with space group $P2_1$ and two molecules in the unit cell of dimensions $a = 7\cdot241$, $b = 13\cdot148$, $c = 11\cdot556$ Å and $\beta = 106\cdot68°$. The absolute configuration of the molecule was derived from the known stereochemistry at the 12-position established in earlier chemical and spectroscopic studies.

Introduction

In our continuing studies on biologically active fungal metabolites, austamide (I) was isolated as a toxic component from Aspergillus ustus (Steyn, 1971).

    II a ; R = H, R' = ---H
    II b ; R = H, R' = ◄ H
    II c ; R = Br, R' = ---H

Prolonged hydrogenation of I gave two diastereo-isomeric tetrahydroaustamides IIa and IIb. Acid hydrolysis of the major product, IIa, liberated S-proline, therefore establishing the 12S-configuration at this newly created chiral centre. The stereochemistry at position 9 was based on the 9S, 12S-configuration of prolyl-2-(1'1'-dimethylallyl)tryptophyldiketopiperazine, an apparent bioprecursor of I. The configuration at the spiro atom, position 2 relative to that of position 9, was based on n.m.r. shift data (Steyn, to be published).

5-Bromo-12S-tetrahydroaustamide (IIc) was prepared for an X-ray crystallographic study in an attempt to substantiate the above conclusions.

Experimental

12S-Tetrahydroaustamide (50 mg) in tetrahydrofuran (2 ml) was treated with pyridinium hydrobromide perbromide (44 mg) in tetrahydrofuran (2 ml). The colourless mixture was concentrated in a stream of nitrogen and the residue partitioned between chloroform and water. The organic phase was concentrated and crystallized from ethanol to yield IIc. [Analysis: Found: C, 54·31; H, 5·60; Br, 17·25; N, 9·05%. $C_{21}H_{24}BrN_3O_3.H_2O$ requires C, 54·63; H, 5·44; Br, 17·06; N, 8·97%].

The bright yellow rhombic crystals are monoclinic with space group $P2_1$ ($0k0$ absent for k odd).

The other crystal data are:

Molecular formula $C_{21}H_{24}BrN_3O_3$
$\lambda(\text{Mo } K\alpha) = 0\cdot70926$ Å
$a = 7\cdot241$ (1) Å
$b = 13\cdot148$ (2)
$c = 11\cdot556$ (1)
$\beta = 106\cdot68$ (30)°
$d_x = 1\cdot46$ g cm^{-3}
$d_m = 1\cdot46$ (measured by flotation in a mixture of bromoform and methanol)
M.W. 446·34
$Z = 2$.

Unit-cell dimensions were calculated from the accurate spot positions measured on a Hilger & Watts four-circle automatic diffractometer using a least-