Data collection: *Kuma Diffraction Software* (Kuma, 1997). Cell refinement: *Kuma Diffraction Software*. Data reduction: *Kuma Diffraction Software*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1261). Services for accessing these data are described at the back of the journal.

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Brucinium Hydrogen Fumarate Sesquihydrate and Brucinium Hydrogen Maleate

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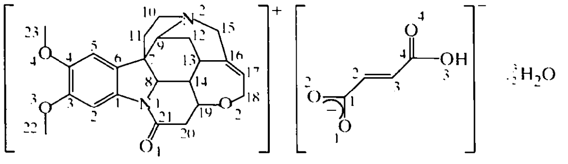
(*Received 3 March 1998; accepted 29 July 1998*)

Abstract

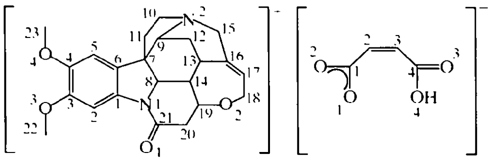
As part of a general study of brucine (alternative name: 2,3-dimethoxystrychnidine-10-one) as a co-crystallizing agent, the structures of its salts with the stereoisomeric fumaric and maleic acids are reported. The packing in the hydrogen fumarate, $C_{23}H_{27}N_2O_4\cdot C_4H_3O_4\cdot\frac{3}{2}H_2O$, is a variation of the corrugated sheet motif common to several brucine crystals, while the hydrogen maleate, $C_{23}H_{27}N_2O_4\cdot C_4H_3O_4$, shows a substantially different motif.

Comment

When structures contain substantial fragments of fixed and known stereochemistry, this may be used as a powerful aid in structure determination (Beurskens *et al.*, 1996). The natural alkaloid, brucine, possesses a well determined stereochemistry, and is therefore potentially very useful as a co-crystallizing agent for large molecules with acidic functions. The hydrogen fumarate, (I), and hydrogen maleate, (II), were obtained as background materials for such a programme. Structures containing brucine have a favoured, but far from universal, mode of packing (Dijksma *et al.*, 1998; Glover *et al.*, 1985; Gould *et al.*, 1984; Pinkerton *et al.*, 1993), in which ribbons of head-to-tail brucinium ions are packed parallel to one another to produce puckered sheets.



(I)



(II)

Both structures consist of equal numbers of brucinium ions and hydrogen fumarate or maleate ions. In (I), the brucinium cations are arranged in ribbons parallel to [010], as in the standard motif. Parallel ribbons (shaded light and dark) related by a twofold rotation axis are shown in Fig. 1. The resulting sheets are normal to [001]; the polarity of the ribbons is the same, but the direction of puckering is opposed. The general effect is to replace the characteristic corrugations with dimples.

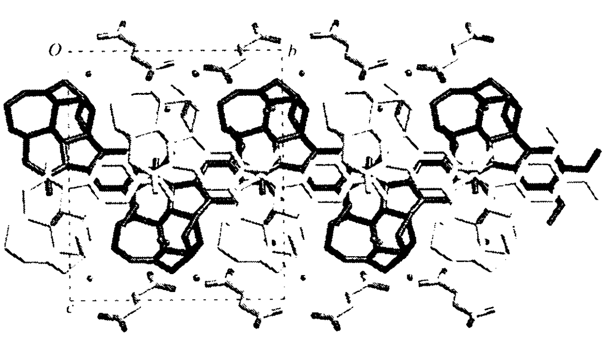


Fig. 1. Packing diagram of (I) viewed down the *a* axis. Short dashed lines indicate hydrogen-bonding interactions. H atoms are omitted for clarity.

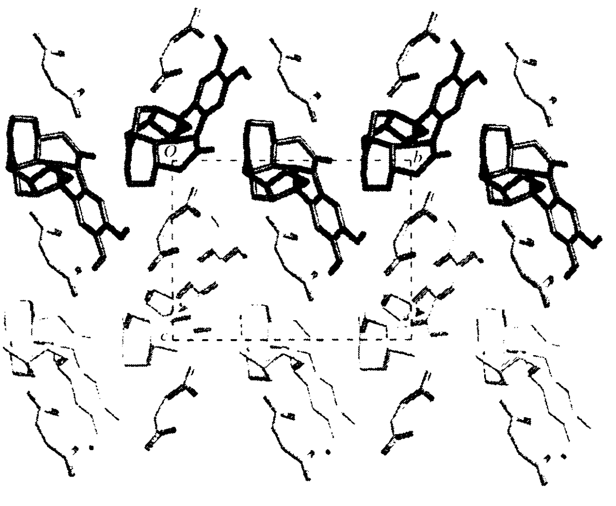


Fig. 2. Packing diagram of (II) viewed down the *a* axis. Short dashed lines indicate hydrogen-bonding interactions. H atoms are omitted for clarity.

Compound (I) is a sesquihydrate: with 50% probability, any asymmetric unit contains either a hydrogen-bonded pair (O1*W* and O2*W*), or O1*W*′ alone, occupying a dimple. Hydrogen fumarate ions form hydrogen-bonded chains about a 2_1 screw-axis between the brucine layers. The N2 of the brucinium forms a bifurcated hydrogen bond to the carboxylic group (O1*F* and O2*F*) of the fumaric acid. The O1 of a brucinium ion in the neighbouring layer is connected indirectly to the fumarate by means of either O1*W* or O1*W*′, which forms hydrogen bonds to both O1 and O1*F*.

Compound (II) is anhydrous and has a substantially different brucine packing. The structure may be derived from the regular packing of ribbons parallel to [010], with alternate residues translated by half a unit cell along [001]. In Fig. 2, the resultant packing is shown with the ribbons shaded light and dark, and is best described as a structure with columns along [100], leaving channels to accommodate the hydrogen maleate ions. These maleate ions have an internal hydrogen

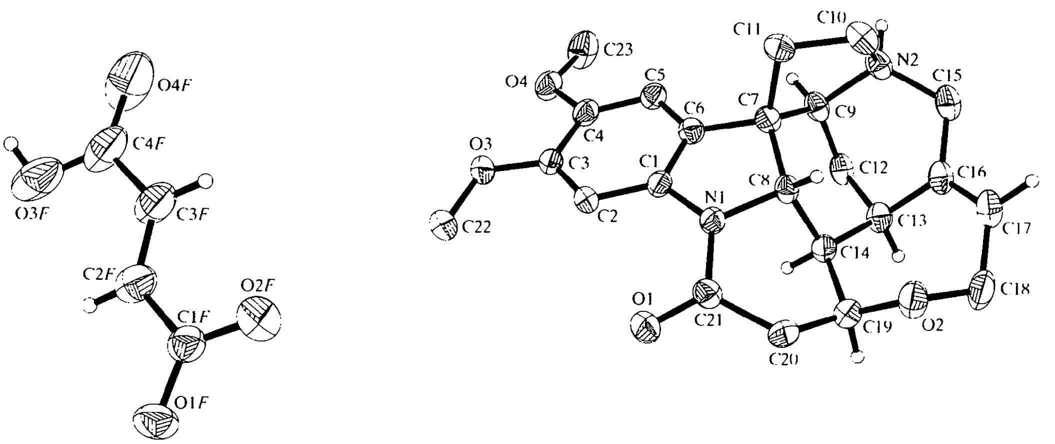


Fig. 3. A view of brucinium and hydrogen fumarate in (I), with 50% probability displacement ellipsoids. All aromatic-H atoms (except H19), the methyl- and methylene-H atoms, and the water molecules, are omitted for clarity.

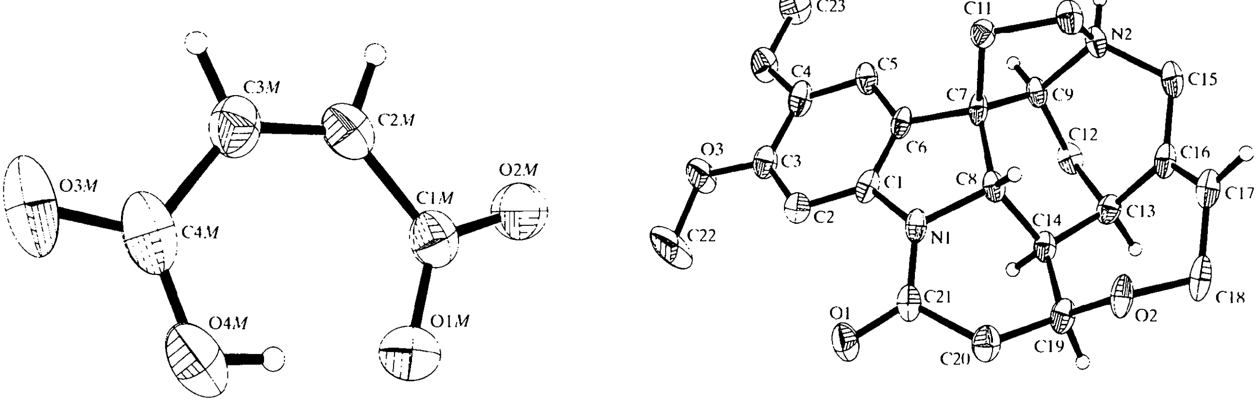


Fig. 4. A view of brucinium and hydrogen maleate in (II), with 50% probability displacement ellipsoids All aromatic-H atoms (except H19), and the methyl- and methylene-H atoms, are omitted for clarity.

bond, and are linked to brucine by the hydrogen bond between N2 and O2*M*. This is the only intermolecular hydrogen bond.

The only part of brucine susceptible to substantial variation is the conformation at the methoxy substituents. The methoxy-ring angles are asymmetric: the bonds to the O atoms do not bisect the C—C—C ring angle but bend toward one another, presumably because of steric interaction between the H atoms of the methyl groups and the ring-H atoms. The four corresponding torsion angles indicate that one of the methoxy groups in each compound is twisted out of the plane of the aromatic ring.

The three bond lengths around the protonated N2 show asymmetry. In both compounds the sequence is N2—C9 > N2—C10 and N2—C15 (Dijksma *et al.*, 1998).

Experimental

Crystals of (I) and (II) were obtained overnight as colourless blocks from aqueous solutions of equimolar mixtures of brucine and fumaric acid and brucine and maleic acid, respectively.

Compound (I)

Crystal data

$C_{23}H_{27}N_2O_4\cdot C_4H_3O_4\cdot\frac{3}{2}H_2O$
$M_r = 537.55$
Monoclinic
$C2$
$a = 14.349\ (3)$ Å
$b = 12.298\ (3)$ Å
$c = 15.173\ (3)$ Å
$\beta = 105.27\ (3)°$
$V = 2582.8\ (9)$ Å^3
$Z = 4$
$D_x = 1.382$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 44 reflections
$\theta = 20–22°$
$\mu = 0.880$ mm^{-1}
$T = 220\ (2)$ K
Block
$0.50 \times 0.27 \times 0.19$ mm
Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986)
ω/θ scans with ω scan width $(0.99 + 0.35\tan\theta)°$
Absorption correction: none
3367 measured reflections
2711 independent reflections

2416 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.012$
$\theta_{\rm max} = 70°$
$h = -17 \rightarrow 16$
$k = -1 \rightarrow 14$
$l = 0 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.096$
$S = 1.051$
2711 reflections
366 parameters

$\Delta\rho_{\rm max} = 0.232$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.259$ e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.00110 (11)

H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0523P)^2 + 1.1904P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.1 (2)

Table 1. *Selected geometric parameters (Å, °) for (I)*

C9—N2	1.530 (4)	C15—N2	1.507 (4)
C10—N2	1.509 (4)		
O3—C3—C2	123.9 (3)	O4—C4—C3	115.4 (3)
O3—C3—C4	115.1 (3)	C3—O3—C22	115.3 (3)
O4—C4—C5	124.7 (3)	C4—O4—C23	116.7 (3)
C1—C2—C3—O3	−178.9 (2)	C2—C3—O3—C22	−2.0 (4)
C2—C3—C4—O4	176.8 (3)	C4—C3—O3—C22	177.4 (3)
O3—C3—C4—C5	175.7 (3)	C5—C4—O4—C23	11.7 (5)
O4—C4—C5—C6	−178.1 (3)	C3—C4—O4—C23	−170.0 (3)

Table 2. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O1*F*$^{\rm i}$	0.92	1.81	2.699 (4)	162.5
N2—H2*A*···O2*F*$^{\rm i}$	0.92	2.41	3.086 (4)	130.0
O3*F*—H3*F*···O2*F*$^{\rm ii}$	0.83	1.76	2.583 (4)	168.5
O1*W*′—H1*WC*···O1$^{\rm iii}$	0.85	2.10	2.937 (10)	168.9
O1*W*′—H1*WD*···O1*F*	0.85	2.01	2.839 (10)	165.2
O1*W*—H1*WA*···O1$^{\rm iii}$	0.85	2.13	2.980 (11)	179.2
O1*W*—H1*WB*···O1*F*	0.85	2.10	2.949 (12)	179.0
O2*W*—H2*WA*···O2*W*$^{\rm iv}$	0.85	2.39	2.996 (18)	129.1
O2*W*—H2*WB*···O1*W*$^{\rm v}$	0.85	1.86	2.702 (14)	168.8
O2*W*—H2*WB*···O1*W*′$^{\rm v}$	0.85	2.45	3.298 (14)	172.7

Symmetry codes: (i) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, -z$; (iii) $1-x, y, 1-z$; (iv) $-x, y, -z$; (v) $x-\frac{1}{2}, \frac{1}{2}+y, z$.

Compound (II)

Crystal data

$C_{23}H_{27}N_2O_4\cdot C_4H_3O_4$
$M_r = 510.53$
Monoclinic
$P2_1$
$a = 7.9410\ (16)$ Å
$b = 13.838\ (3)$ Å
$c = 11.370\ (2)$ Å
$\beta = 111.27\ (3)°$
$V = 1164.3\ (4)$ Å^3
$Z = 2$
$D_x = 1.456$ Mg m^{-3}
D_m not measusred

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 24 reflections
$\theta = 20–22°$
$\mu = 0.898$ mm^{-1}
$T = 220\ (2)$ K
Block
$0.45 \times 0.38 \times 0.30$ mm
Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986)
ω/θ scans with ω scan width $(0.9 + 0.35\tan\theta)°$
Absorption correction: none
2289 measured reflections
2213 independent reflections

2024 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\rm max} = 70°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity decay: <3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.177$
$S = 1.091$
2213 reflections
338 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1412P)^2 + 0.1949P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.560$ e Å^{-3}
$\Delta\rho_{\min} = -0.511$ e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.0073 (19)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.4 (4)

Table 3. *Selected geometric parameters (Å, °) for (II)*

C9—N2	1.536 (5)	C15—N2	1.504 (6)
C10—N2	1.501 (6)		
O3—C3—C2	124.3 (5)	O4—C4—C3	114.3 (4)
O3—C3—C4	114.9 (4)	C3—O3—C22	116.7 (4)
O4—C4—C5	125.8 (5)	C4—O4—C23	116.4 (4)
C2—C3—O3—C22	−14.6 (9)	C5—C4—O4—C23	−2.3 (8)
C4—C3—O3—C22	166.4 (7)	C3—C4—O4—C23	179.0 (5)

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···O2*M*ⁱ	0.92	1.78	2.671 (6)	161.7
O4*M*—H4*M*···O1*M*	0.83	1.64	2.471 (7)	175.6

Symmetry code: (i) $x - 1, y, z$.

Brucine is a naturally occurring molecule with a well established stereochemistry and no atoms other than C, H, N and O; this enables the structure to be based on a unique set of data with no Friedel equivalents, as anomalous data will make no significant difference to the absolute structure refinement. This also contributes to the low reflection-to-parameter ratio.

Two atoms show rather high displacement parameters, namely, O4*F* in (I) and C22 in (II). Their slight disorder could not be modelled satisfactorily, but it does show clearly, in the case of O4*F*, that there is no stabilizing hydrogen bond, and for C22, that the conformation of methoxy groups is variable, as mentioned above. The site occupancies for O1*W*/O2*W* and O1*W*′ were refined to values near 50%, then fixed for consistency. All H atoms were placed, with the H atoms on O1*W*, O1*W*′ and O2*W* being placed to give an acceptable hydrogen-bonding network, except for H2*WA* which was found in the difference map.

For both compounds, data collection: *DIF*4 (Stoe & Cie, 1990*a*); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1990*b*); program(s) used to solve structures: *DIRDIF*96 (Beurskens, 1996); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *Cerius*^{2} (Molecular Simulations Inc., 1997) and *SHELXTL* (Sheldrick, 1994) for (I); *Cerius*^{2} (Molecular Simulations Inc., 1997) for (II). For both compounds, software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1243). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1951–1954

Ethyl 3-Hydroxybenzo[*b*]furan-2-carboxylate

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(*Received 8 July 1998; accepted 29 July 1998*)

Abstract

Molecules in the title compound, $C_{11}H_{10}O_4$, occur as centrosymmetric dimers, which lie in parallel planes separated by about 1 Å. Both intra- and intermolecular hydrogen bonding occurs across the –OH···O=C groups of the dimer, in a rhombic arrangement. The non-H atoms are effectively planar in each monomeric unit, with the ethyl groups lying in an extended *trans* configuration. A theoretical study of the equilibrium structures of both the monomeric and dimeric units was made by SCF (self-consistent field) methods with a double-ζ basis set. The monomeric and dimeric structures obtained are very similar to each other, and to the observed structure.