

Brucine and two solvates

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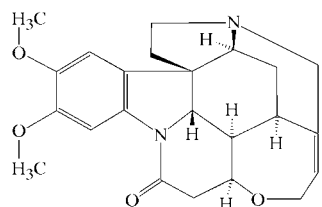
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The crystal structures of brucine (2,3-dimethoxystrychnidin-10-one), $C_{23}H_{26}N_2O_4$, brucine acetone solvate, $C_{23}H_{26}N_2O_4 \cdot C_3H_6O$, and brucine 2-propanol solvate dihydrate, $C_{23}H_{26}N_2O_4 \cdot C_3H_7O \cdot 2H_2O$, have been determined. Crystals of brucine and its 2-propanol solvate dihydrate exhibit similar monolayer sheet packing, whereas crystals of the acetone solvate adopt a different mode of packing, as brucine pillars. The solvent appears to control the brucine self-assembly on the basis of common donor–acceptor properties of the surfaces.

Comment

In a recent paper (Białońska & Ciunik, 2004), we reported molecular recognition during racemic resolution by fractional crystallization. Different donor–acceptor capabilities of *N*-benzoyl- (Gould & Walkinshaw, 1984) and *N*-phthaloyl- α -alanine determine various brucine or strychnine self-assemblies, which recognize the *D*- or *L*-enantiomer of alanine derivatives. These crystallizations were carried out from mixtures containing an alkaloid, a racemic alanine derivative and a solvent. Since the solvent plays an important role in molecular recognition and therefore in racemic resolution (Lehn, 1995; Jacques *et al.*, 1991), our further studies focused on the influence of the solvent on the crystallization of brucine. For clarity, we used acetone and 2-propanol as solvents, which have similar sizes but different chemical properties.



(I)
(II) = (I) · C_3H_6O
(III) = (I) · $C_3H_7O \cdot 2H_2O$

Views of the molecules, with the atom-numbering schemes, are presented in Fig. 1. The crystal structure of unsolvated brucine, (I), consists of corrugated monolayer sheets of

brucine (Fig. 2) that are parallel to the (001) plane. The *c* cell dimension reflects the distance between neighbouring brucine sheets. Methoxy atoms O2 and O3, and the arene ring, are involved as acceptors in weak hydrogen bonds, stabilizing the

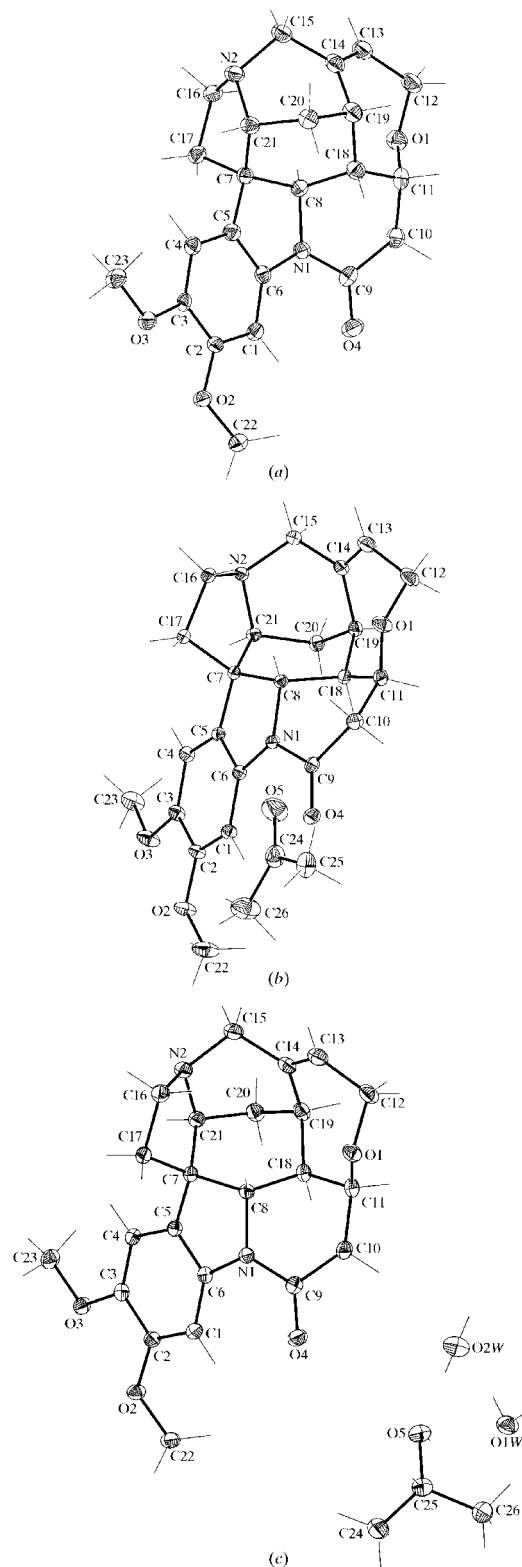


Figure 1
Views of the crystal structures of (a) (I), (b) (II) and (c) (III), with the atom-numbering schemes. Ellipsoids are shown at the 50% probability level.

structure of the monolayer sheet. Carbonyl atom O4 and amine atom N2 are acceptors of weak hydrogen bonds to adjacent parallel sheets.

The molecular packing of brucine acetone solvate, (II), consists of brucine pillars (Fig. 3). The carbonyl O atom of the brucine molecule, in the centre of the pillar, is an acceptor of weak C—H···O hydrogen bonds. Amine N and methoxy O atoms on the pillar surface are able to accept weak hydrogen bonds from adjacent pillars. Cavities between the arene rings protruding from a pillar are occupied by acetone molecules, contributing to C—H··· π hydrogen bonds that form between acetone methyl groups and aromatic rings of brucine molecules.

Crystals of brucine 2-propanol solvate dihydrate, (III), are similar to those of (I) and brucine ethanol solvate dihydrate (Glover *et al.*, 1985) in that they adopt brucine monolayer sheet packing. The methoxy O atoms and arene ring of the

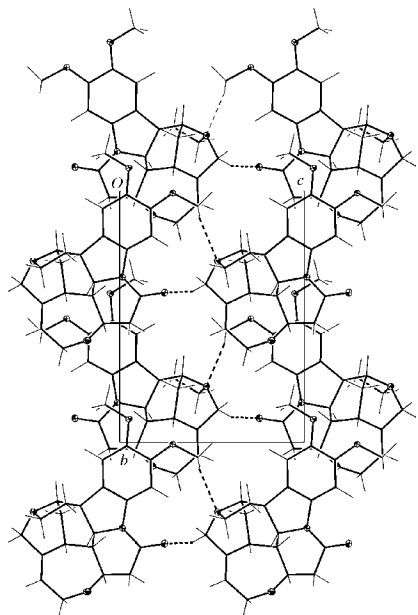


Figure 2
The brucine monolayer sheets in (I). Dashed lines represent C—H···N and C—H···O(carbonyl) hydrogen bonds.

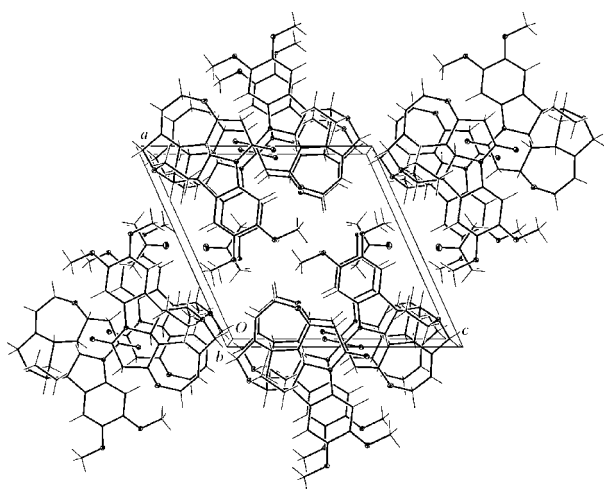


Figure 3
The molecular packing of (II).

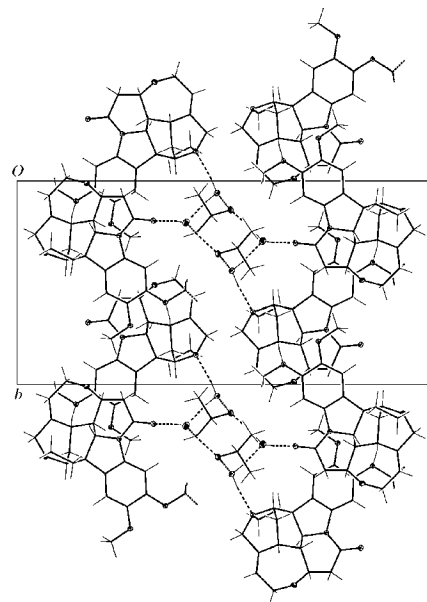


Figure 4
The molecular packing of (III). Dashed lines represent O—H···N and O—H···O hydrogen bonds.

brucine molecule play a similar role to those in (I), where C—H···O(methoxy) and C—H··· π (arene) contacts stabilize the sheets. However, in (III), antiparallel neighbouring brucine sheets are separated by columns of solvent molecules (propanol and water) extending through the crystal channels (Fig. 4). Carbonyl atom O4 and amine atom N2 are directed towards the channel, and both participate as acceptors in hydrogen bonds with solvent ribbons (Table 1).

The brucine monolayer sheets in (I) are linked by weak hydrogen bonds that are relatively easily displaced by stronger hydrogen bonds with co-crystallizing compounds, such as those in (III) and in various other crystals (Gould & Walkinshaw, 1984; Glover *et al.*, 1985; Dijkstra *et al.*, 1998; Boiadjiev *et al.*, 1992; Pinkerton, 1993; Tanaka *et al.*, 2001). While 2-propanol may form strong hydrogen bonds with hydroxy groups by both donation and acceptance, the acetone molecule is only able to form weak interactions, with the carbonyl O atom acting as an acceptor. The different donor–acceptor capabilities of 2-propanol and acetone lead to different brucine self-assembly design. However, the donor–acceptor capabilities of brucine self-assembled surfaces in crystals of (II) and (III) correspond well to the donor–acceptor properties of acetone and 2-propanol, respectively. Strong hydrogen bonds involving the carbonyl O and amine N atoms are possible because of the structure of the brucine monolayer surface in (III). Closure of the carbonyl O atom into the pillar in (II) causes its surface to give limited possibilities for acceptance of hydrogen bonds and to be susceptible to weak intermolecular interactions.

Experimental

Crystals of brucine (POCh, Poland), (I), were grown from acetone solution. After dissolving the crystals of (I) by heating in the mother liquid, crystals of brucine acetone solvate, (II), were obtained. Crystals of brucine 2-propanol solvate dihydrate, (III), were grown

from 2-propanol solution. Crystals of (I), (II) and (III) suitable for X-ray diffraction measurements were obtained at room temperature.

Compound (I)

Crystal data

$C_{23}H_{26}N_2O_4$ $D_x = 1.382 \text{ Mg m}^{-3}$
 $M_r = 394.46$ Mo $K\alpha$ radiation
 Monoclinic, $P2_1$ Cell parameters from 2231 reflections
 $a = 7.992 (2) \text{ \AA}$ $\theta = 3.5\text{--}27.0^\circ$
 $b = 12.704 (3) \text{ \AA}$ $\mu = 0.10 \text{ mm}^{-1}$
 $c = 9.471 (2) \text{ \AA}$ $T = 100 (2) \text{ K}$
 $\beta = 99.68 (3)^\circ$ Plate, colourless
 $V = 947.9 (4) \text{ \AA}^3$ $0.30 \times 0.25 \times 0.25 \text{ mm}$
 $Z = 2$

Data collection

Kuma KM-4 CCD diffractometer $R_{\text{int}} = 0.032$
 ω scans $\theta_{\text{max}} = 27.0^\circ$
 5627 measured reflections $h = -10 \rightarrow 10$
 2126 independent reflections $k = -16 \rightarrow 11$
 2021 reflections with $I > 2\sigma(I)$ $l = -12 \rightarrow 12$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0318P)^2 + 0.4569P]$
 $R[F^2 > 2\sigma(F^2)] = 0.040$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.089$ $(\Delta/\sigma)_{\text{max}} = 0.001$
 $S = 1.10$ $\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$
 2126 reflections $\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$
 262 parameters
 H-atom parameters constrained

Compound (II)

Crystal data

$C_{23}H_{26}N_2O_4 \cdot C_3H_6O$ $D_x = 1.323 \text{ Mg m}^{-3}$
 $M_r = 452.54$ Mo $K\alpha$ radiation
 Monoclinic, $P2_1$ Cell parameters from 7521 reflections
 $a = 12.765 (3) \text{ \AA}$ $\theta = 3.7\text{--}30.0^\circ$
 $b = 7.1360 (14) \text{ \AA}$ $\mu = 0.09 \text{ mm}^{-1}$
 $c = 13.686 (3) \text{ \AA}$ $T = 100 (2) \text{ K}$
 $\beta = 114.35 (3)^\circ$ Block, colourless
 $V = 1135.8 (4) \text{ \AA}^3$ $0.25 \times 0.25 \times 0.20 \text{ mm}$
 $Z = 2$

Data collection

Kuma KM-4 CCD diffractometer $R_{\text{int}} = 0.023$
 ω scans $\theta_{\text{max}} = 30.0^\circ$
 14 702 measured reflections $h = -17 \rightarrow 17$
 3499 independent reflections $k = -7 \rightarrow 10$
 3412 reflections with $I > 2\sigma(I)$ $l = -19 \rightarrow 19$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 0.1072P]$
 $R[F^2 > 2\sigma(F^2)] = 0.030$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.081$ $(\Delta/\sigma)_{\text{max}} = 0.002$
 $S = 1.05$ $\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$
 3499 reflections $\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
 298 parameters
 H-atom parameters constrained

Table 1
 Hydrogen-bonding geometry (\AA , $^\circ$) for (III).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
$O5\text{--}H5\cdots O1W^i$	0.88	1.88	2.7622 (18)	179
$O1W\text{--}H11W\cdots O2W$	0.92	1.90	2.8206 (18)	173
$O1W\text{--}H12W\cdots N2^{ii}$	0.90	1.92	2.8158 (17)	173
$O2W\text{--}H21W\cdots O4^{iii}$	0.86	1.99	2.8449 (17)	176
$O2W\text{--}H22W\cdots O5$	0.90	1.86	2.7474 (17)	170

Symmetry codes: (i) $\frac{1}{2} + x, \frac{3}{2} - y, -z$; (ii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $1 + x, y, z$.

Compound (III)

Crystal data

$C_{23}H_{26}N_2O_4 \cdot C_3H_8O \cdot 2H_2O$ Mo $K\alpha$ radiation
 $M_r = 490.58$ Cell parameters from 6099 reflections
 Orthorhombic, $P2_12_12_1$ $\theta = 3.2\text{--}27.5^\circ$
 $a = 7.9297 (3) \text{ \AA}$ $\mu = 0.10 \text{ mm}^{-1}$
 $b = 12.3289 (7) \text{ \AA}$ $T = 100 (2) \text{ K}$
 $c = 25.1631 (10) \text{ \AA}$ Block, colourless
 $V = 2460.06 (19) \text{ \AA}^3$ $0.50 \times 0.40 \times 0.40 \text{ mm}$
 $Z = 4$
 $D_x = 1.325 \text{ Mg m}^{-3}$

Data collection

Kuma KM-4 CCD diffractometer $R_{\text{int}} = 0.028$
 ω scans $\theta_{\text{max}} = 27.5^\circ$
 16 487 measured reflections $h = -10 \rightarrow 10$
 3185 independent reflections $k = -12 \rightarrow 16$
 3019 reflections with $I > 2\sigma(I)$ $l = -31 \rightarrow 32$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0468P)^2 + 0.3452P]$
 $R[F^2 > 2\sigma(F^2)] = 0.029$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.074$ $(\Delta/\sigma)_{\text{max}} = 0.001$
 $S = 1.06$ $\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$
 3185 reflections $\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$
 316 parameters
 H-atom parameters constrained

H atoms were found in $\Delta\rho$ maps. H-atom parameters were refined with isotropic displacement parameters and were fixed before the final cycles of refinement. Friedel pairs were merged before the final refinement. The absolute configurations of (I), (II) and (III) were chosen on the basis of the known absolute configuration of brucine.

For all compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2001); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 1999); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1174). Services for accessing these data are described at the back of the journal.

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